

The Chemistry of Phenolic Resins

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**THE FORMATION, STRUCTURE, AND REACTIONS
OF PHENOLIC RESINS AND RELATED PRODUCTS**

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TO MY WIFE

Lola K. Martin

P R E F A C E

This book was written to present in a single source the chemistry not only of present-day phenolic resins but also of a great many related products that may be obtained as more or less pure compounds. This has not been attempted before, although various phases of the subject have been covered in separate reviews. Sections of several excellent books such as Carswell's on phenoplasts, Ellis's on synthetic resins, and Walker's on formaldehyde have dealt with the chemistry of phenolic resins. Hultzsich's *Chemie der Phenolharze*, in particular, provides a detailed treatment of the chemistry of phenolic resins, but unfortunately it is available only in German. Much of the chemistry of the cyclic products formed by the reactions of phenols with aldehydes or ketones has been covered in the series *Heterocyclic Compounds* by Elderfield. Blicke's review of the Mannich reaction (*Organic Reactions*, Vol. I) includes phenols as one of a large group of compounds that undergo this reaction. Fuson and McKeever's review of chloromethylation in the same volume also mentions the use of phenols in this reaction.

The selection of material for the present book has been purely arbitrary on my part, being governed by my personal evaluation as to its importance or by my own interest in the reaction. This may have resulted in the exclusion of some material that others might have included or the inclusion of some that others might have omitted. However, it is hoped that the omissions have not been too frequent or my errors in judgment too serious. Besides, I had to draw the line somewhere if the book was ever to be completed.

Because of the commercial importance of the phenol-aldehyde resins large portions of the book have been devoted to these products. Details relating to current manufacturing practice and the end uses for the products have been adequately covered elsewhere and have been omitted, except for cursory references, from the present treatment. On the other hand, the chemistry of their preparation and the structure of the products obtained have been discussed in detail.

To explain the reactions encountered during the cure of a phenolic resin has been a difficult but challenging problem. Owing to the extreme complexity of the reactions it is not surprising that conflicting interpretations of the data or even apparently conflicting data appear in the literature. As far as practical, the literature has been reviewed and the reactions that seem best supported by the evidence available have been indicated. It is hoped that such treatment will focus attention on those aspects of the problem where gaps in our knowledge exist and will thereby stimulate further research in the field.

A discussion of the reactions that occur between phenols and aldehydes or ketones and a third reagent has been placed in a separate chapter. Reactions that lead to cyclic products have also been treated separately. A chapter has been devoted to the reactions of the more common phenol-aldehyde and ketone products with some common reagents. As an aid to the research worker the more important phenol-aldehyde or phenol-ketone products such as the phenol alcohols, dihydroxydiphenylalkanes, and dihydroxydibenzyl ethers have been listed in table form along with their melting points and pertinent references. Finally a summary of the results from reaction-rate studies has been given in a chapter at the end of the book.

The literature in the field under discussion is very extensive and some of it dates back a hundred years. Even though an exhaustive survey of the literature has not been attempted, an effort has been made to cover the major contributions in each field and to provide an ample list of references should the reader desire more detailed information. I have relied most heavily on the material published in the technical journals in recent years but have included references to patents where a more or less basic contribution has been described or where data were not available from other sources.

Much of this book has been written with the resin chemist clearly in mind, but even those sections dealing with the preparation and cure of the phenolic resins, which are of paramount interest to him, have been approached from the point of view of the organic chemist. More often than not, variables in a reaction have been considered as to how they affect the chemistry involved rather than how they affect the performance of the product in its end use. Although the resin chemist or research worker in polymer chemistry may find this book most useful, it is hoped that the organic chemist, the student, the engineer, or even the casual reader who wishes to familiarize himself with the subject matter will also find it of interest.

I have had valuable help from many sources in preparing this book. I am indebted to Dr. K. Adler, University of Stockholm; Dr.

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R. W. M.

Emeryville, California
March, 1958

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C H A P T E R O N E

Introduction

Organic chemists of the last century were primarily interested in the preparation of pure compounds composed of a single molecular component. The polymeric and resinous materials which were seldom amenable to conventional methods of purification and characterization attracted little attention. With this background it is not surprising that the first studies of the phenol-aldehyde reaction, made by Baeyer around 1870, were devoted to the synthesis of crystalline products.

The first crystalline products obtained were the dihydroxydiphenylalkanes. They attracted some attention as dye intermediates and in medicinal preparations since these applications could tolerate the then expensive raw materials required for their synthesis. The hydroxymethylphenols, or phenol alcohols as they are commonly called, were obtained independently by Lederer and Manasse around 1894. No large-scale uses for these materials were developed at this time, although saligenin, *o*-hydroxymethylphenol, was found to have analgesic properties.

The resins which were often obtained in spite of the deliberate precautions taken to avoid their formation were regarded as nuisances by the early workers and were discarded as useless "gunks." It is perhaps a little ironical that these so-called gunks came to exceed in commercial importance all other phenol-aldehyde or phenol-ketone products. In defense of the early workers it should be pointed out that phenol and formaldehyde were not yet available in commercial quantities or at a price that could be tolerated in a resin and also that resins were not an important phase of the then infant chemical industry.

The first patents covering resinous phenol-aldehyde condensation products were issued around the turn of the century. DeLair, Smith, and Lebach were particularly active during this period. Their efforts were directed primarily toward the preparation of substitutes for shellac, which was then in short supply. Although none of their prod-

ucts were entirely successful, knowledge of the work along these lines undoubtedly played a part in attracting the genius of Dr. Leo Baekeland to the materials. Dr. Baekeland's studies of the phenol-aldehyde reaction began around 1905, and the results of his early experiments were announced to the world at an American Chemical Society meeting in 1909.

Baekeland made so many valuable contributions to the field of phenolic resins that it would be hazardous to pick a single contribution as being his greatest. He sought from the beginning to achieve better control over the resin preparation, and he emphasized the importance of limiting the amount of catalyst. He introduced the addition of wood flour and other fillers to overcome the inherent brittleness of the resins. His famous "Heat and Pressure" patent described a means for bringing about the rapid cure of a molding composition in a shape predetermined by the shape of the mold. Pressures greater than the vapor pressure of the water evolved during the curing process were employed to prevent blistering and the formation of voids in the molded article. The use of high temperatures permitted rapid curing cycles and hence made the process attractive commercially.

A major contribution was made about 1911 by Aylsworth who recommended hexamethylenetetramine as a curing agent for the permanently soluble and fusible resins now known as the novolacs. The novolacs were readily prepared and were hard, grindable, easily handled resins that could be stored for long periods without deterioration. The products cured with hexamethylenetetramine were found to have superior electrical properties. As a result they soon found widespread application for the fabrication of parts for electrical equipment.

Meanwhile other applications for phenolic resins were developing. By combining large quantities of formaldehyde with phenol under alkaline conditions viscous syrups were obtained that were suitable for casting. For many years these materials were used widely for the fabrication of handles, buckles, ornaments, and novelties of various types, but they have now been largely displaced by the thermoplastic resins. The casting resins still find use in preparing molds and dyes where steel molds are not required. Phenolic resins were also employed in the preparation of laminates, surface coatings, and adhesives, and as binders for abrasive wheels. Most of these applications were suggested by Baekeland, but they often had to wait a number of years for large-scale applications to develop. Phenolic resins are now being employed as the binder for wood-waste products, a potentially large-volume application. Another field where phenolic resins

are being introduced is in the foundry resins. Here they serve as binders for the sand in sand cores and shell moldings.

Beginning around 1910 it was found that phenolic resins became compatible with drying oils if they were first fluxed with rosin or fossil resins. When properly combined with drying oils or resins these "modified" phenolic resins, even in small amounts, imparted improved hardness and resistance to the surface coatings. The pure or "100%" phenolic resins, unmodified with natural resins but in combination with drying oils, were introduced around 1929. Oil solubility was conferred on the phenolic resins by employing phenols having oleophilic groups in the form of alkyl or aryl substituents. Ion-exchange resins and tanning agents based on phenol-aldehyde condensates have also been developed.

The growth of the phenolic resin industry in the United States probably may best be appreciated by inspection of production figures. Unfortunately figures are not available for the early years, but it has been estimated that around 5 million pounds of resins were produced in 1921. By 1943 production had jumped to over 144 million pounds according to United States Tariff Commission reports. The Tariff Commission figures for 1953 showed a total volume of phenolic and all other tar acid resins of nearly 485 million pounds, well over a threefold increase in 10 years.

Once the utility of the resinous phenol-aldehyde products had been established, studies, usually of an empirical nature, were initiated in an effort to develop resins suited to each new application. It may be safely said that interest in the technology of the resins during the early days of the phenolic resin industry far overshadowed interest in the chemistry involved or in the pure chemicals that might be obtained by proper control of reaction conditions. However, as the resin technology developed and the applications for the resins became more specialized it became necessary to know in ever-increasing detail the factors controlling the properties of the resins, their mode of formation, speed of cure, etc. Because of the complexity of the resins, the resin chemists were forced to employ pure compounds as models for their studies. Partly as an outgrowth of the efforts with the model compounds and partly because of a renewed interest in phenol-aldehyde chemistry in general, better ways for preparing the pure compounds and a better understanding of their chemistry developed. As often happens, once the new compounds became available applications for them developed.

Of the more or less pure compounds available from the phenol-aldehyde or ketone reaction, the dihydroxydiphenylalkanes, or bis-

phenols, are probably the most important commercially. The bisphenols derived from alkyl phenols of proper structure have become important as antioxidants for rubber, plastics, petroleum products, vegetable oils and fats, etc. Chlorinated bisphenols are used in germicidal soaps and in sterilizing solutions. Still other bisphenols are employed in various pharmaceutical preparations, pesticides, oil additives, and many other applications. One of the largest single applications for bisphenols has been as intermediates for the manufacture of polyepoxide resins. These resins are prepared by the reaction of a bisphenol with epichlorohydrin and caustic.

Besides the bisphenols several other phenol-aldehyde or phenol-ketone products have been offered either in commercial or pilot-plant quantities. The Mannich bases derived from phenols have been employed directly or as intermediates for the preparation of emulsifying agents, detergents, corrosion inhibitors, additives for pickling baths, and as textile assistants. They also function as catalysts for promoting the cure of polyepoxide resins. Several sun-screening agents, a variety of oil additives, surface-active agents, dye intermediates, and many other specialty products are based on products that may be obtained as more or less pure compounds by the condensation of phenols with aldehydes or ketones.

The above list of applications, though far from complete, serves to emphasize the great variety and importance of the non-resinous phenolic products. It now seems evident that what began as an interest in crystalline compounds and shifted almost exclusively to an interest in resinous products has reached a point where both types of products are being actively exploited. The prospects for growth in both fields appear bright.

C H A P T E R T W O

Phenol Alcohols

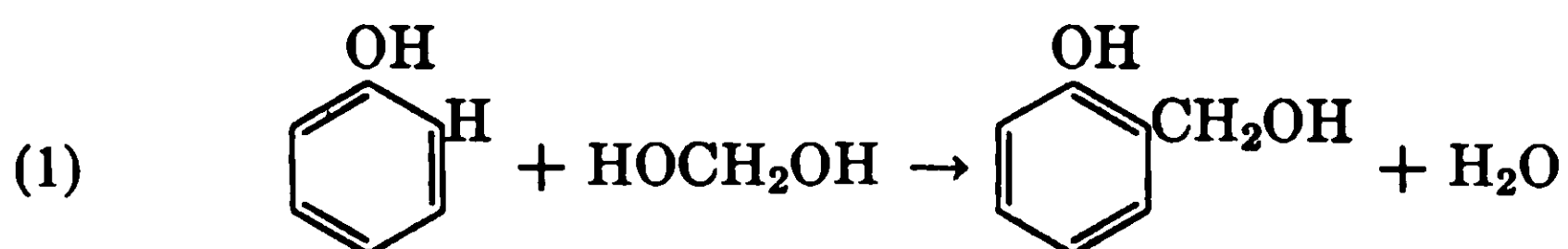
Phenols combine with aldehydes or ketones to form a variety of products. The nature of the product depends on the choice of the phenol and the aldehyde or ketone and on the conditions of reaction. The two most common reactions are the addition of methylol groups to the phenol and the subsequent formation of a methylene derivative of the phenol. The simple products possessing methylol groups are commonly referred to as phenol alcohols; the short-chain two-ring methylene derivatives are known as dihydroxydiphenylmethanes. The long-chain resins, whose commercial importance overshadows all other phenol-aldehyde products, are polynuclear products derived from the simple methylol and methylene derivatives mentioned above. It is therefore logical to start a discussion of phenol-aldehyde chemistry with these two basic types of derivatives. As phenol alcohols are intermediates to the methylene derivatives, they will be considered first.

The phenol alcohols occupy a position of major importance among the numerous products derived from phenols and aldehydes or ketones. Besides being intermediates in most, if not all, resinous phenolic products, they represent in themselves an interesting class of highly reactive organic chemicals. Baeyer^{1*} was the first to study the phenol-aldehyde condensation reactions in detail and is credited with establishing their general nature. However, it remained for Lederer² and Manasse³ to show that phenol alcohols could be prepared by the direct reaction of phenols and aldehydes. With our present knowledge, it is now possible to prepare phenol alcohols from nearly all phenols having at least one free *ortho* or *para* ring hydrogen atom. Because of their commercial importance and high reactivity, the phenol alcohols based on formaldehyde will be considered in greatest detail.

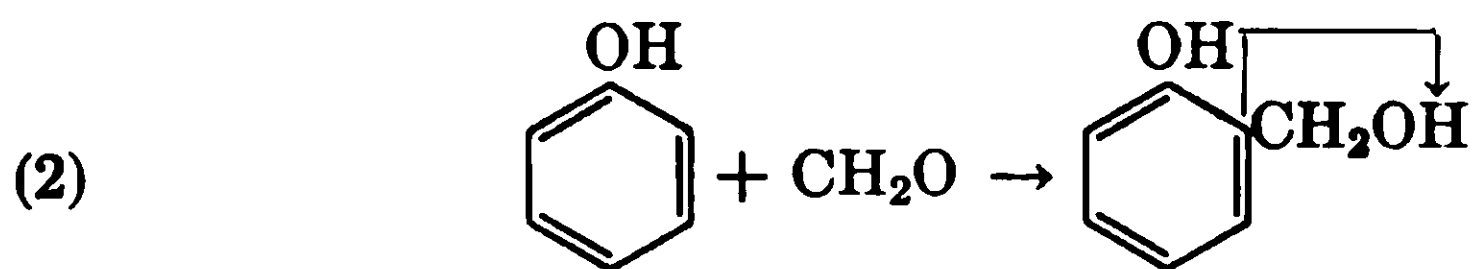
* The citations will be found at the end of the respective chapters.

MECHANISM OF REACTION

The formation of phenol alcohols by the addition of aldehydes to phenols is catalyzed by both acidic and basic materials, the mechanism being dependent on the type of catalyst used. Under basic conditions Manasse found that reaction occurred *ortho* and *para* to the phenolic hydroxyl group and suggested that formaldehyde may react in aqueous solution as methylene glycol.⁸ The methylol group would then be formed by the elimination of water between an *ortho* or *para* hydrogen of the phenol and a hydroxyl group of the methylene glycol, equation 1.

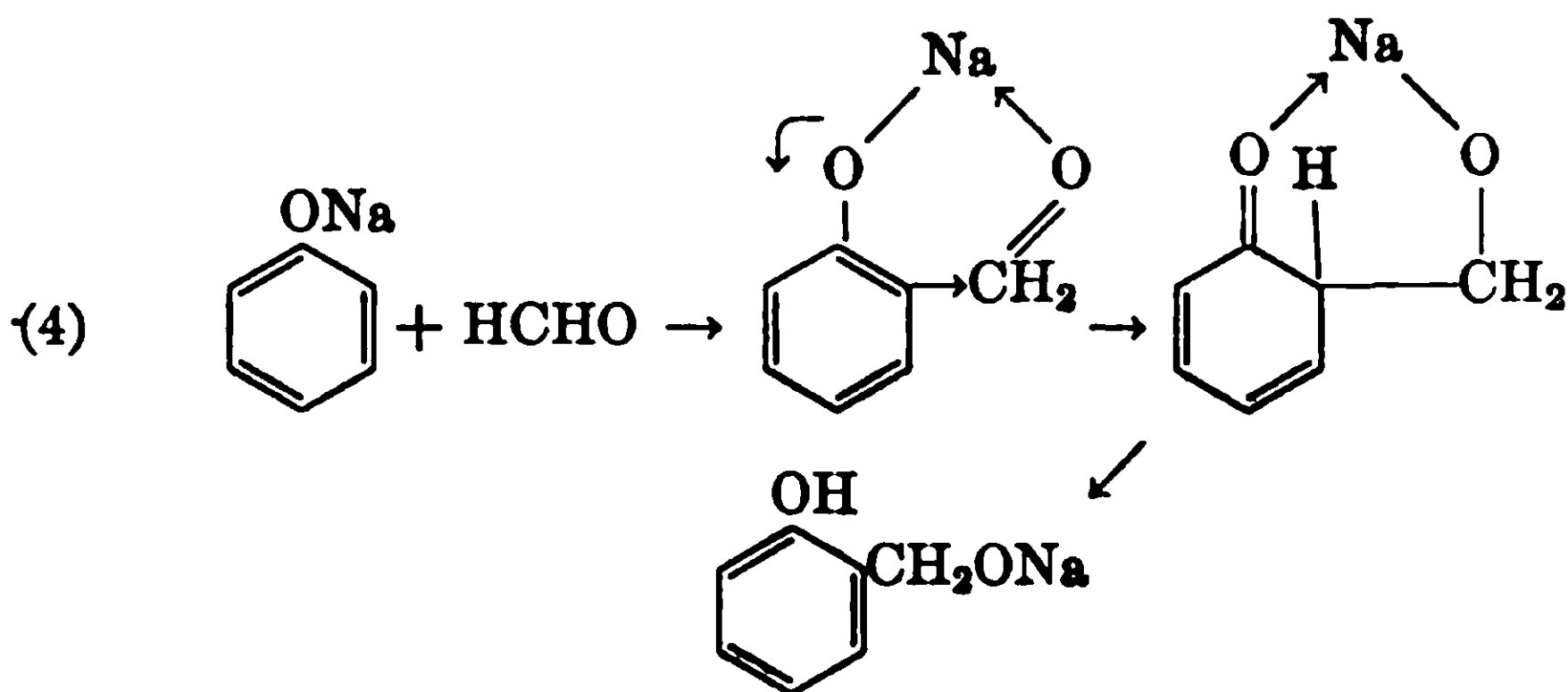
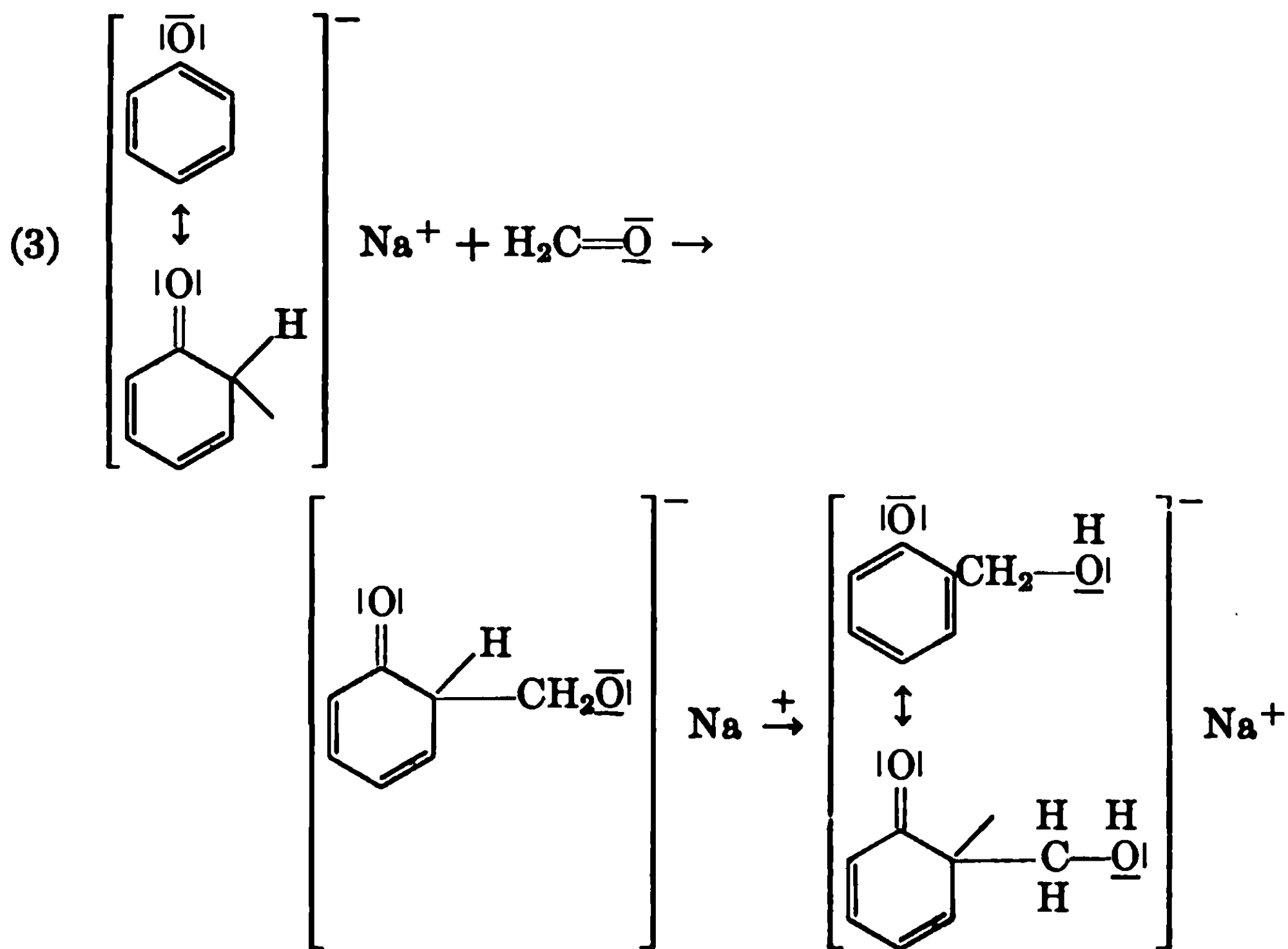


This is undoubtedly an oversimplification, and Manasse apparently recognized its inadequacy for he suggested an alternative mechanism involving an aldol type of reaction in which formaldehyde forms the alcohol group with an *ortho* or *para* hydrogen of the phenol, equation 2.

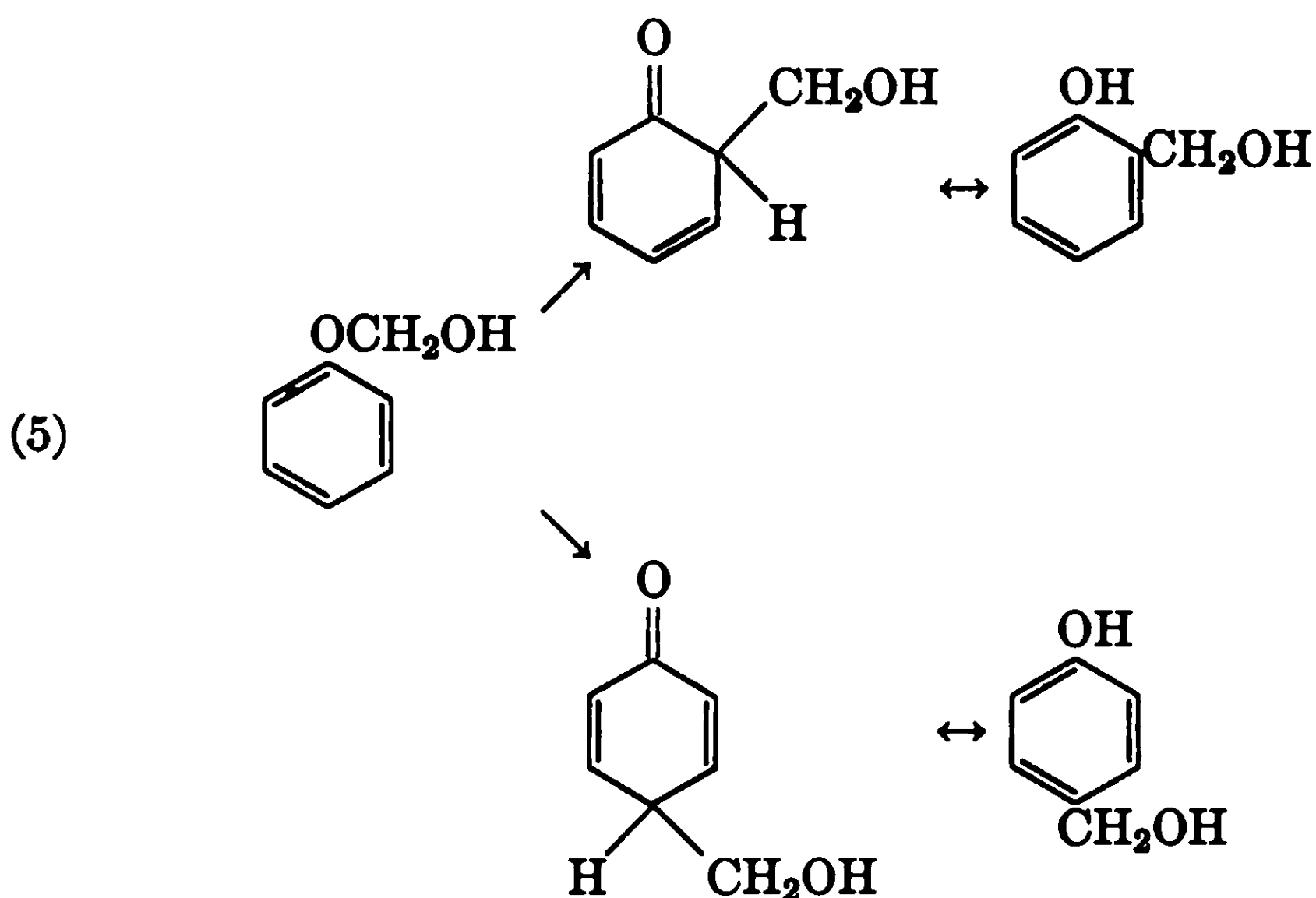


The present theories, though much extended and refined, still view the alkaline catalyzed reaction as an aldol type of condensation.⁴⁻⁶ Hultsch's^{7,8} picture of the steps involved incorporates most of the essential features of the modern point of view, equation 3. The driving force for the reaction is derived from the nucleophilic nature of the phenate ion^{6,8,9} and is dependent on the concentration of hydroxyl ions above a *pH* of about 5.⁶ (See Chapter 10.)

Somewhat earlier, in a private communication to Caesar and Sachanen,¹⁰ Price suggested that the phenol may react with formaldehyde in the presence of an alkaline catalyst to form a chelate ring, which, on intramolecular rearrangement, would give an *ortho* alcohol, equation 4. This mechanism does not account for *para* alcohols whose formation is often slightly favored over the *ortho* alcohols with strong alkaline catalysts. (Ehlers claims that in caustic solution six molecules of saligenin may complex with one sodium ion.¹¹)



Walker¹² has suggested that the phenol first forms a hemiacetal, which then undergoes tautomeric rearrangements of the type indicated, equation 5. In proposing this mechanism, Walker draws an analogy between the formation of phenol alcohols and the formation of methylol derivatives of aldehydes and ketones. Hemiformals of phenols have not been reported, but methyl phenyl formal has been obtained from an acid-catalyzed reaction of phenol with formalin containing methanol.¹⁴⁻¹⁵ This has been advanced as indirect evidence for the existence of hemiformals of phenol. On the other hand certain substituted aldehydes, such as chloral, form moderately stable hemiacetals



with phenols.¹⁸ The stability of the hemiacetal appears to be related to the reactivity of the phenol since *p*-cresol gives a more stable hemiacetal with chloral than phenol. The formation of the hemiacetal is catalyzed by basic materials such as potassium carbonate. As early as 1926 Chattaway¹⁷⁻¹⁸ proposed that hemiacetals were intermediates in the formation of benzodioxans from phenols and chloral. Bender¹⁸ also favors the general theory of reaction involving the formation of a hemiacetal followed by rearrangement of the hemiacetal to a methylolphenol.

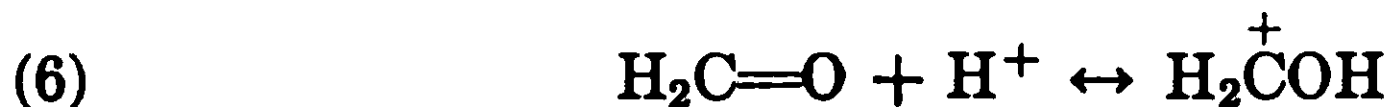
Another argument for acetal or hemiacetal formation is the stabilization of formaldehyde against the Cannizzaro reaction by phenol. Under alkaline conditions formaldehyde is rapidly converted to methanol and formic acid, but in the presence of phenol the reaction is almost eliminated even at reflux temperature²⁰ except where more than half a mole of caustic is present per mole of phenol.¹⁸ It has been suggested that the formaldehyde is tied up in some manner by the phenol, possibly as a hemiformal. Among the early workers, Baekeland and Bender²¹ and Claisen,²² and more recently Euler and Kispoczy,²³ have expressed the view that reaction of formaldehyde with phenols occurs first at the phenolic hydroxyl group.

An argument sometimes advanced in support of a reaction involving the phenolic hydroxyl group is that methylol groups are not added under alkaline conditions when the phenolic hydroxyl group is blocked by esterification or etherification. This argument is untenable since the driving force for the reaction depends on the nucleophilic nature

of the phenate ion. Therefore, phenolic ethers and esters would not be expected to react with formaldehyde under alkaline conditions.

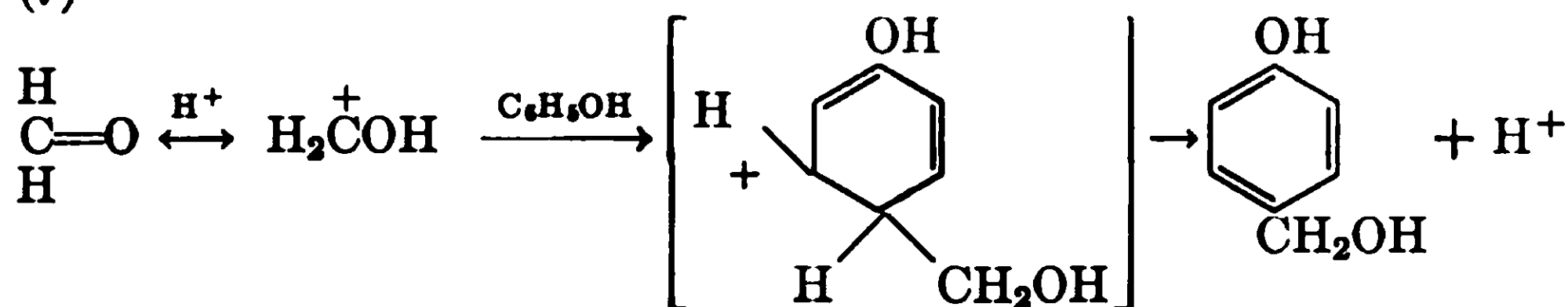
Under acidic conditions phenol alcohols are susceptible to condensation reactions which result in the formation of dihydroxydiphenylmethanes and resins. Therefore acids ordinarily are not employed as catalysts in the synthesis of phenol alcohols except with inactive phenols. It is widely accepted, however, that phenol alcohols, or an ionic derivative thereof, are intermediates in the formation of methylene derivatives of phenols. The most convincing evidence for this view has been the detection or isolation of phenol alcohols from acid-catalyzed reaction mixtures.²⁸⁻³⁰ By the use of chromatographic techniques, Reese³¹ has detected phenol mono- and polyalcohols among the products of the reaction of phenol with formaldehyde in the presence of a small amount of hydrochloric acid. Finn, James, and Standen³² have obtained similar results, and Freeman³³ has found *o*- and *p*-hydroxybenzyl alcohol in a reaction catalyzed with sulfuric acid.

With acidic catalysts, the catalyst appears to react with the aldehyde to form an active intermediate,^{8,9,34} equation 6:



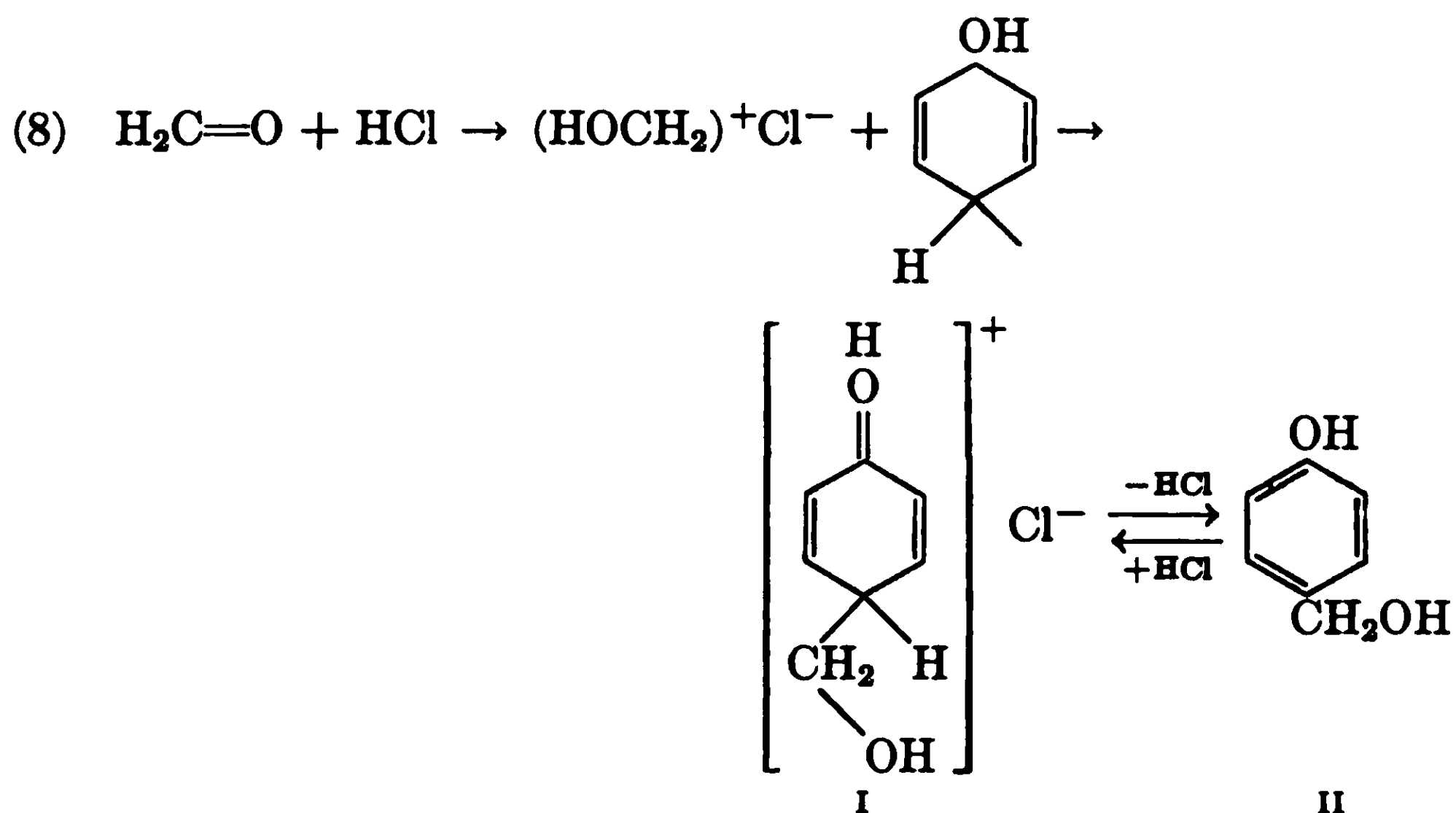
According to Price¹⁰ the ionic intermediate then attacks the phenol as shown in equation 7.

(7)

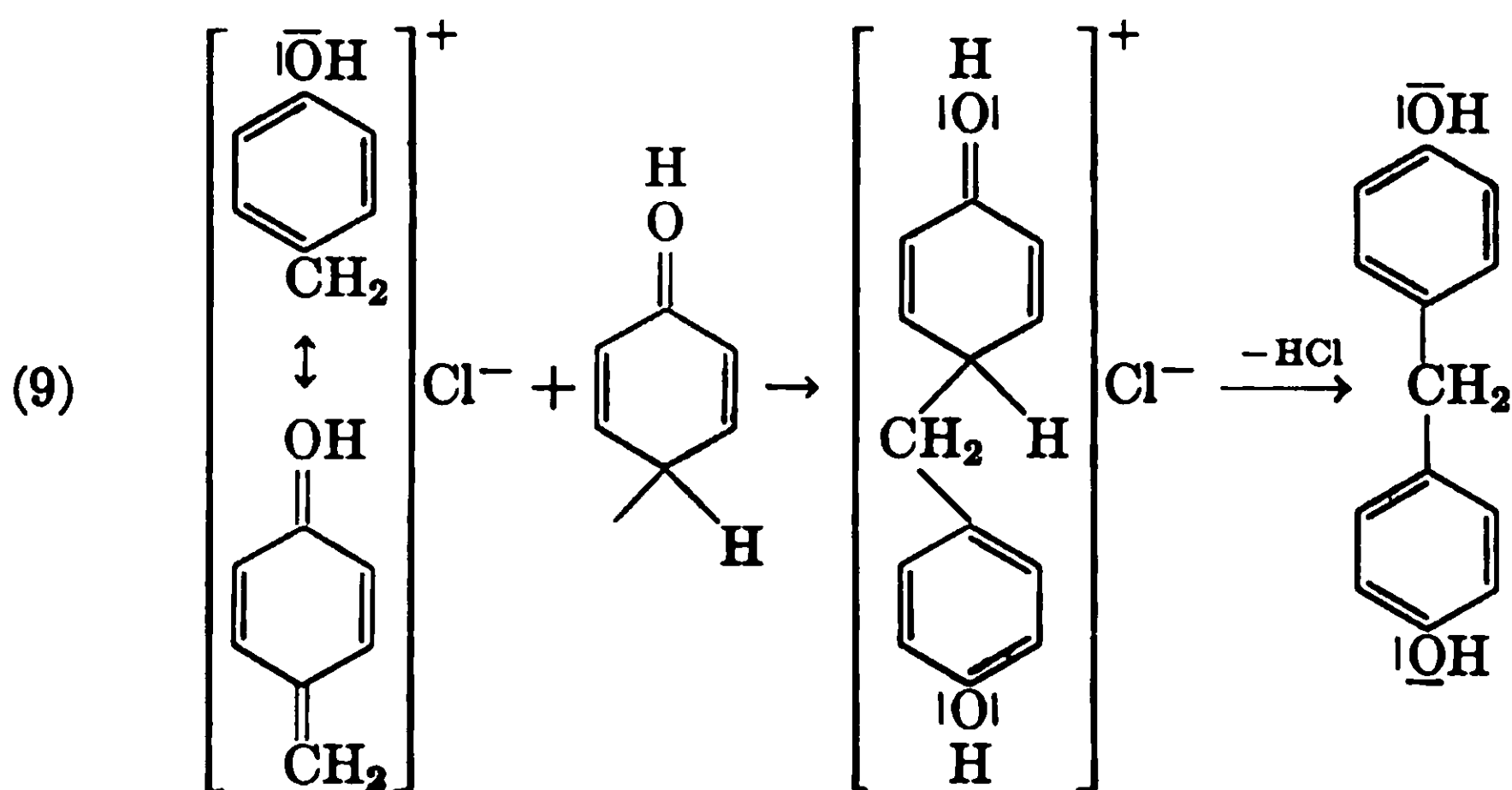


The driving force for the reaction is derived from the electrophilic nature of the formaldehyde-proton complex and appears to be proportional to the concentration of hydrogen ions below a *pH* of about 3.6.⁶ This has been given as evidence for the above mechanism.^{6,33}

The primary reaction postulated by Hultsch^{7,36} also assumes the formation of an adduct between the phenol and a cation, obtained by the addition of a proton from the condensation medium (such as HCl) to the formaldehyde, equation 8. By the loss of HCl from adduct I,



the formation of phenol alcohols under dilute acidic conditions would be explained. However, Hultzsich thinks that usually adduct I loses water, forming a cation. The cation then reacts with the oxonium form of another phenol molecule and a dihydroxydiphenylmethane is obtained, equation 9. If this theory is correct, then a phenol alcohol is



not necessarily an intermediate in the formation of dihydroxydiphenylmethane. Further, the relative ease of hydrolyzing or dehydrating adduct I must be strongly influenced by the nature of the substituents on the phenol nucleus as well as by reaction conditions. Otherwise, it would be difficult to explain the preparation of phenol alcohols from certain phenols while others undergo almost instantaneous resinification under similar conditions.

The catalytic effect of ammonia or primary and secondary amines on the formation of phenol alcohols is poorly understood. Even the existence of phenol alcohols in reactions catalyzed by ammonia was doubted for many years but has now been confirmed by Martin⁸⁷ and Ruderman.⁸⁸ It is known that when used in equimolar quantities secondary amines and formaldehyde reacts with phenols to form dialkylaminomethylphenols (see Chapter 5). With catalytic quantities of the amine, it appears likely that similar or identical products would be formed until the amine was consumed. The products, being tertiary amines, may conceivably function as weak alkaline catalysts. Primary amines also react with phenols and formaldehyde. Both monoalkylaminomethylphenols and bis(hydroxybenzyl)amines have been obtained.⁸⁹⁻⁹⁴ Either type of product may be capable of acting as a basic catalyst for the addition of methylol groups. The very favorable charge-sharing possibilities of amine-formaldehyde products, such as $R_2N-CH_2^+ \leftrightarrow R_2N^+=CH_2$, also should be considered when attempting to explain the catalytic activity of the amines.⁴⁵

With ammonia the reactions involved are even more complex than with amines, and the true catalyst is even more obscure. Ammonia reacts almost instantaneously with formaldehyde to form hexamethylenetetramine, probably through an intermediate methylol derivative of the ammonia. Hexamethylenetetramine is capable of forming addition complexes with phenols, such as hexatriphenol.⁴⁶ By heating such complexes or simple mixtures of phenols with hexamethylenetetramine bis and tris(hydroxybenzyl)amines are formed.^{3, 47-53} It is possible that these secondary and tertiary amines function as weak basic catalysts for phenol alcohol formation, but conclusive evidence has not been reported to support this theory. The independent synthesis of some of the intermediate phenolic amines and a study of their catalytic action on phenol alcohol formation would undoubtedly provide much information of value in connection with this problem.

EFFECT OF SUBSTITUENTS ON REACTIVITY OF PHENOLS

The substituents on a phenol play an important part in the over-all chemistry of phenol-aldehyde products. In general, phenols react with aldehydes and ketones only at ring positions located *ortho* and *para* to the phenolic hydroxyl group. This is due to the very strong *ortho*- and *para*-directing influence of a phenolic hydroxyl group. The functionality of a phenol, a very important concept in resin chemistry, is equal to the total number of *ortho* and *para* positions relative to the phenolic hydroxyl group that are available for reaction. The relation

between functionality, structure, and the maximum number of phenol alcohols that theoretically may be synthesized from several representative phenols is given in Table I. The formation of several isomeric

Table I. Functionality vs. Number of Phenol Alcohols

Phenol	Function- ality of Phenol	Number of Mono- alcohols	Number of Di- alcohols	Number of Tri- alcohols	Number of Tetra- alcohols	Total Number Alcohols
2,4-Dimethylphenol	1	1				1
2,6-Dimethylphenol	1	1				1
<i>p</i> -Cresol	2	1	1			2
<i>o</i> -Cresol	2	2	1			3
2,3-Dimethylphenol	2	2	1			3
2,5-Dimethylphenol	2	2	1			3
3,4-Dimethylphenol	2	2	1			3
3,5-Dimethylphenol	3	2	2	1		5
Phenol	3	2	2	1		5
Resorcinol	3	2	2	1		5
<i>m</i> -Cresol	3	3	3	1		7
Hydroquinone	4	1	3	1	1	6
Catechol	4	2	3	2	1	8

phenol alcohols from a single phenol accounts for the large number of different methylol derivatives possible from certain phenols.

Besides limiting the number of positions available for reaction in a phenol, substituents affect the orientation of an entering methylol group and cause activation or deactivation of the parent phenol. A methylol group normally does not add at a position *meta* to a phenolic hydroxyl group, but it may add at either an *ortho* or *para* position or at both positions, depending on the nature and the location of the substituent on the phenol. Owing to the effects of substituents on the activation or deactivation of a phenol, substituted phenols may show pronounced differences in their reactivity with aldehydes and ketones.

In general, an *ortho-para* directing group located *meta* to the phenolic hydroxyl enhances the reactivity of the phenol. For example, *m*-cresol adds formaldehyde at nearly three times the rate of phenol, and 3,5-xyleneol has nearly eight times the reactivity of phenol in the early stages of reaction.⁵⁴ As would be expected, resorcinol is extremely reactive, owing to the strong activation received from two phenolic hydroxyl groups located *meta* to one another. If an *ortho-para* directing group is introduced *ortho* or *para* to the phenolic hydroxyl group, the activation is not as noticeable as in the *meta* position and in many cases the substituted phenol may be less reactive than phenol itself. However, the methylene group in the *ortho* positions between two phenols imparts great reactivity.

Halogens, though *ortho*- and *para*-directing, deactivate all positions on the benzene ring. Therefore, it is not surprising to find that halogenated phenols react somewhat sluggishly with aldehydes.

All *meta*-directing groups tend to inactivate the benzene ring, and phenols containing these groups show decreased activity towards aldehydes. Such phenols react very slowly, if at all, with formaldehyde under alkaline conditions. On the other hand with catalysts which are sufficiently acidic phenol alcohols have been obtained even with the nitro phenols. This difference in reactivity with type of catalyst is probably associated with the nature of the attacking group under the two sets of conditions.

According to Sprung,⁵⁴ the introduction of a methylol group has about the same effect on the rate of formaldehyde uptake as a methyl group in the same position. This conclusion was based on rate studies on uptake of formaldehyde by saligenin as compared to *o*- and *p*-cresols, using triethanolamine as catalyst. In the presence of strong alkalies, such as the alkali metal hydroxides, the addition of a methylol group in certain positions appears to enhance the activity of the phenol. This conclusion is supported by several independent observations, one of which is the strong tendency for many phenols to form polyalcohols even at a low ratio of formaldehyde to phenol (see page 20). For example, Goldblum⁵⁵ has shown that trimethylolphenol is formed in large amounts when much less than 3 moles of formaldehyde are allowed to react with a mole of aqueous sodium phenate (see Table II). Finn and Lewis⁵⁶ proposed that, with phenols having substituents

Table II. Effect of Phenol-Formaldehyde Ratio on Yield of Trialcohol

Molar ratio, phenol/formaldehyde	1/0.5	1/1	1/1.5	1/2.0	1/2.5
Per cent of sodium trimethylolphenate	3.38	9.24	22.16	31.00	40.70
Moles sodium trimethylolphenate/ mole sodium phenate	0.036	0.121	0.339	0.548	0.812

Reproduced by permission of the author, K. B. Goldblum.

in the *para* or *meta* positions, the introduction of a methylol group into one *ortho* position facilitated the entry of a second methylol group in the other *ortho* position. They found that 3,5-xyleneol gave either the *para*-mono alcohol or the *ortho-ortho* dialcohol. All attempts to prepare the *ortho* monoalcohol were unsuccessful. With *para*-substituted phenols the ease with which the dialcohol is formed, even at 1 to 1 ratio, is well established.

Sprengling and Lewis⁵⁷ attempted to gain an insight into the effect

of methyl and methylol groups on the reactivity of a phenol by comparing the pK values of the substituted and unsubstituted phenols. It was reasoned that, the higher the proportion of a given phenol present in a reaction mixture as anions, the greater its reactivity. However, the very substituents causing the change in acidity of the phenol may also influence the rate of substitution. This limited their study to rather simple substituents such as methyl and methylol groups where differences in reactivity due to substituent, per se, would be relatively small. Ultraviolet absorption spectra were used to determine the percentage of the phenol in the anion form. Measurements were made in dilute buffered solutions of known pH .

According to these authors a methylol group should be weakly *meta*-directing and ring-deactivating. On the basis of acidity alone, *p*-methylolphenol should be more reactive than either cresol or saligenin. However, Sprengling and Lewis consider that this effect is probably more than balanced by the fact that the whole ring is deactivated by the methylol group. In saligenin, the effect of a hydrogen bond involving the phenolic proton comes into play. This should tend to keep the phenolic hydroxyl group turned into the plane of the ring, which would favor the resonance transfer of a negative charge to the ring in the undissociated form, increasing its reactivity especially in the *para* position. However, this resonance stabilization would not extend to the anion. Since 2,6-dimethylolphenol is not only the most acid and would have its phenolic hydroxyl held to the plane of the ring, it should be the most reactive of the methylol derivatives of phenol as far as reaction with formaldehyde is concerned.

The relative reactivities of the various methylolphenols have since been determined quantitatively by Freeman and Lewis,⁸⁸ and the predictions made by Sprengling and Lewis in general have been confirmed. An *ortho* position in phenol is slightly less reactive than a *para* position, but in saligenin the reverse is true. The introduction of a methylol group in the *ortho* position enhances the reactivity of the remaining positions. This makes 2,6-dimethylolphenol by far the most reactive component of a phenol-formaldehyde reaction mixture. (See Chapter 10.)

ORIENTATION OF METHYLOL GROUPS

Assuming that both an *ortho* and a *para* position relative to the phenolic hydroxyl group are available for reaction, the question frequently arises as to where the methylol group will enter the benzene ring. As early as 1894 Lederer² stated that the entry of a

methylol group in either the *ortho* or the *para* position could be controlled by the proper choice of catalyst. He planned to publish the details of his discovery, but this was never done.

Auwers⁵⁰ reported in 1907 that strong alkaline catalysts favored the formation of the *para*-methylol derivative of 2,5-xylenol. More recently Sprengling and Freeman⁶⁰ studied the reaction of phenol with formaldehyde at a ratio of 1 to 1.4, using sodium hydroxide as catalyst. When reaction was complete, the phenolic hydroxyl groups of the phenol alcohols were etherified by treatment with dimethyl sulfate, and the methylol groups were oxidized to carboxylic acid groups according to a scheme published by Meyer.⁶¹ The acids were then separated, and the amounts recovered were used to estimate the quantity of each phenol alcohol present in the original mixture. An inspection of the data shows that the *para*-monoalcohol and the 2,4-dialcohol were the major products (Table III).

Table III. Reaction Products of the Phenol-Formaldehyde Reaction

Components of Reaction Product	Mole % Present
Phenol	5-10
<i>o</i> -Methylolphenol	10-15
<i>p</i> -Methylolphenol	35-40
2,4-Dimethylolphenol	30-35
2,6-Dimethylolphenol	None
2,4,6-Trimethylolphenol	4-8

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Martin⁶² made a similar study using 2.1 moles of formaldehyde per mole of phenol. At this ratio, also, the *para* monoalcohol and the 2,4-dialcohol were found in greatest quantity. At the higher formaldehyde to phenol ratio, a small quantity of the 2,6-dialcohol also was detected.

Care must be taken to avoid misinterpretation of the results of the above experiments. The concentration of any particular phenol alcohol in a phenol-formaldehyde reaction mixture at any moment depends not only on the rate of formation of the phenol alcohol but also on its rate of disappearance due to further reactions. These factors have been studied in detail by Freeman and Lewis,⁶³ and a graph showing the formation and disappearance of each phenol alcohol capable of formation from phenol by the addition of one, two, or three methylol groups⁶ to sodium phenate has been reproduced on page 257. This graph shows the accumulation of the *para*-monoalcohol and the

2,4-dialcohol after several hours of reaction. An explanation for the shape of the various curves is found in the relative rates of reaction of the *ortho* and *para* positions of the phenol alcohols with additional formaldehyde (see page 256).

The rate data show that in general the *para* position of phenol has a slightly greater affinity for formaldehyde than an *ortho* position. This does not necessarily mean that the *para*-alcohol will always be found in greater quantity. With phenol, having two *ortho* positions available for each *para* position, the advantage of the greater reactivity of the *para* position is overcome and the *ortho*-monoalcohol is produced at a greater rate than the *para*-monoalcohol. As a result, saligenin will be the first phenol alcohol to appear in appreciable quantity in a phenol-formaldehyde reaction mixture. Owing to further reaction its concentration will remain essentially static, and it will be the first phenol alcohol to disappear. The *p*-methylophenol will appear in appreciable quantity somewhat later than saligenin, since it is formed at a slower rate. As it is less reactive than saligenin or phenol, the quantity of this phenol alcohol will increase steadily until the supply of phenol is exhausted. 2,4-Dimethylophenol will be formed still later in the reaction. It will accumulate in the system and become a major component, owing to its decreased reactivity for the addition of more formaldehyde. Because of the very high reactivity of 2,6-dimethylophenol, it will not be found in appreciable quantities at any time during the reaction. These results are in excellent agreement with the findings described by Sprengling and Freeman and by Martin.

The joint reaction of formaldehyde and a secondary amine with phenol leads to an amine analog of a phenol alcohol. The data indicate that most of these amine analogs are attached to the phenol at a position *ortho* to the phenolic hydroxyl group if this is possible, although exceptions may be found.⁶⁵⁻⁶⁶ As yet conclusive data have not been published to show that catalytic quantities of amines cause the entry of a methylol group preferentially at an *ortho* position.

In reactions catalyzed by ammonia, Martin⁶⁷ recovered 4-methylol- and 2,4-dimethylophenol. Here again the rates of formation of the phenol alcohols and their rates of further reaction determine the quantity of phenol alcohol to be found at any instant. Therefore the isolation of the alcohols listed above does not necessarily mean that their formation is favored by ammonia. Seto⁶⁷ found bis and tris(hydroxybenzyl)amines and also phenol alcohols in a phenol-formaldehyde reaction mixture prepared with ammonia as the catalyst.

Only with phenols containing negative groups are acids used to prepare phenol alcohols. With hydrochloric acid as catalyst, o-nitro-

phenol gave a mixture of monomethylol derivatives in which the *ortho* and *para* compounds were found in the ratio of 1 to 3.⁶⁸

The position at which a methylol group becomes attached to a phenol may be affected by steric factors. A very large *meta* substituent will frequently cause the methylol group to enter at the *ortho* position on the opposite side of the ring. For example, Jones and Robson⁶⁹ report that when 3-pentadecylphenol was reacted in alkaline solution with formaldehyde a 98% yield of 6-methylol-3-pentadecylphenol was obtained.

An indication of the effect of a solvent on the location of an entering methylol group came from Finn, Lewis, and Megson.⁷⁰ It was found that 3,5-xyleneol reacts with formaldehyde in aqueous caustic to form the *p*-monoalcohol, also obtained earlier by Auwers.⁶⁹ When the reaction was carried out in ethanol with sodium ethoxide as catalyst, the 2,6-dialcohol was formed.

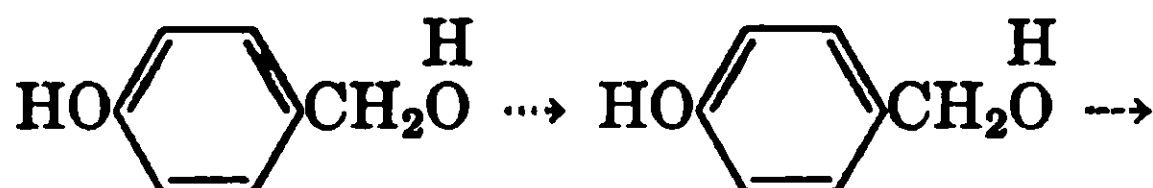
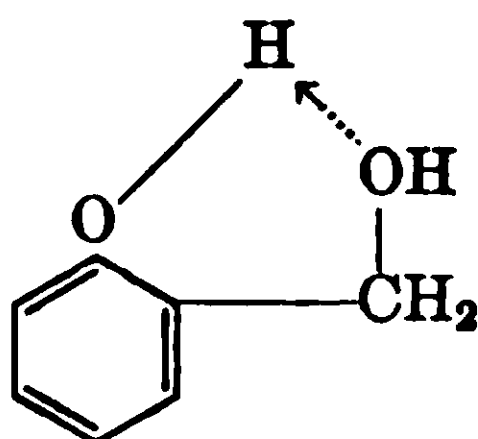
Auwers claims that saligenin will change to *p*-hydroxybenzyl alcohol when heated.⁷¹ However, a straight isomerization of one phenol alcohol to another seems unlikely. On the other hand phenol alcohols may lose formaldehyde which could then recombine with the liberated phenol at any position on the phenol available for reaction. The amount of new phenol alcohol formed by such a series of reactions will be small since resin formation and other reactions will consume most of the phenol alcohol. Unlike the methylol derivatives of phenol those of melamine and urea appear to be in dynamic equilibrium with free formaldehyde and melamine and urea.⁷²

STABILIZATION OF PHENOL ALCOHOLS

Experience has shown that phenol alcohols may be prepared and handled only under certain limited conditions. Under less favorable conditions they are rapidly converted to resins. Hultzs^{3, 66, 73} believes that at moderate temperatures and in the absence of catalysts a phenol alcohol is stabilized by hydrogen bonding between the methylol and phenolic hydroxyl groups. Under conditions which would destroy such bonding, e.g., heat, acids, and polar solvents, the phenol alcohols would become reactive and the phenolic hydroxyl group which had once served as a stabilizing factor would now activate the methylol groups. It is not yet possible to determine how much of the increased activity of a phenol alcohol at elevated temperature or in the presence of acids and polar solvents is due to the destruction of hydrogen bonding and how much is due to the normal effects of heat,

acids, etc., on reaction rates in general. However, the theory merits some discussion.

Where possible, stabilization of the phenol alcohol is presumed to occur by formation of a six-membered ring, but intermolecular bonding is also postulated. The two types of bonding are shown below.



The bonds would not be as strong as a coordinate or covalent linkage, but they could have considerable strength, according to Hultzsch.⁶⁶ Huckel⁷⁴ had previously suggested that the hydroxyl groups in saligenin should be capable of intramolecular hydrogen bonding and Richards and Thompson⁷⁵ have obtained experimental evidence for such bonding from infrared data. As might be expected they found a profound difference in the amount of bonding at 20° and 100°C.

The importance of a strong donor atom, such as oxygen, to the stability of a methylol group is shown, according to Hultzsch, by comparing the products formed by condensing aniline and phenol with formaldehyde. Under alkaline conditions formaldehyde reacts with aniline at the amino group, but in place of a stable methylol derivative a polymeric azomethine is formed.⁷⁶ Under similar conditions phenol would give a phenol alcohol. Hultzsch attributes the formation of a stable methylol derivative of phenol, and the lack of such a derivative in the case of aniline, to the oxygen atom which allows for stabilization of the methylol group by hydrogen bonding. This argument is weak since it is now recognized that an amine group also is capable of hydrogen bonding.

If it is assumed that the formation of a six-membered ring is favored over intermolecular bonding, then a *p*-methylolphenol should show greater reactivity towards condensation than its corresponding *ortho* isomer. In general this is true, although the difference in reactivity sometimes may be very small.^{8, 77, 78} The data presented below point up some of the more interesting findings.

p-Hydroxybenzyl alcohol is considerably more reactive towards condensation than saligenin, according to Bender.^{79, 80} Others claim that *p*-hydroxybenzyl alcohol is more easily resinified in solution but is somewhat more stable than its *ortho* isomer in crystalline form.^{77, 78} Reese^{80a} has made a detailed study of the condensation of each of the

five possible phenol alcohols of phenol. The condensations were run in acidic and alkaline solution at 70°C. and in a melt at 110°C. The phenol alcohols were heated alone and also in the presence of free phenol. After a predetermined heating period the products of the reaction were separated by two-dimensional chromatography. By comparing the R_f values of the fractions with those of known compounds, where available, and by considering the known effects of structure on the R_f values where reference compounds were not available, Reese was able to assign either definite or probable structures to the various products. With 2,4-dimethylolphenol where both an *ortho* and a *para* methylol group are available for reaction Reese found that coupling usually occurred at the *para* position. Even with trimethylolphenol, where there are two *ortho* methylol groups for each *para* methylol group, coupling at the *para* position occurred most frequently.

Among the substituted phenols, 2,6-dimethyl-4-methylolphenol is converted to a methylene derivative more easily than 2,4-dimethyl-6-methylolphenol. It also has been observed that it is somewhat more difficult to prepare a dialcohol without resinification from an *o*-alkylphenol than it is from an *p*-alkylphenol.

When considering the stability of a phenol alcohol in light of the theory of stabilization through hydrogen bonding, trimethylolphenol is interesting to consider. The attraction of the two *ortho* methylol groups of trimethylolphenol for the phenolic hydroxyl group would exclude essentially all stabilization of the *para* methylol group by intermolecular bonding with a phenolic hydroxyl group. If the stability of the compound depended solely on hydrogen bonding, it would be expected to be extremely unstable if not impossible to isolate.⁸⁸ However, the compound has been prepared both directly by reaction of formaldehyde with phenol and indirectly by the reduction of appropriate derivatives of phenol.^{87, 88, 81-84} It is sufficiently stable to permit recrystallization from low-boiling solvents and extended storage in crystalline form although it is not very stable in aqueous alkaline solution.

In spite of certain discrepancies, some of which were mentioned above, the theory explains, at least qualitatively, why *para* phenol alcohols are generally more reactive towards condensation than their *ortho* isomers. It also explains the decreased stability of phenol alcohols with several methylol groups.

It is somewhat surprising in view of this theory to find that phenol alcohols and resoles (phenolic resins with methylol groups) show their greatest stability at a pH that is distinctly acidic where the amount of hydrogen bonding should be reduced over that found at

neutrality. For example, it has been reported that resoles based on phenol have optimum stability at a *pH* of 3.8 to 4.5 and resoles derived from resorcinol are most stable at a *pH* of 3 to 4.^{8,88-88} In contrast to these results Bender reports that the resinification of *p*-hydroxybenzyl alcohol is rapid at a *pH* of 4.⁸⁰ Bender's findings are more in line with predictions based on the above theory.

The effects of hydrogen bonding on the activity of phenol alcohols towards resinification should not be confused with its effects on the addition of formaldehyde. Under conditions where a mole of caustic is present for each mole of phenol alcohol, Freeman and Lewis⁵⁸ found as much as an 11-fold difference in the reactivity of *p*-methylophenol and 2,6-dimethylophenol with formaldehyde. The differences in reactivity of these phenol alcohols towards formaldehyde as related to differences in hydrogen bonding has been discussed by Freeman and Lewis.

POLYALCOHOL FORMATION

The reaction of formaldehyde with the more reactive phenols in the presence of strong alkalies (sodium hydroxide, sodium carbonate, barium hydroxide, quaternary ammonium bases, etc.) is characterized by a strong tendency toward polyalcohol formation.⁸⁹⁻⁹⁰ This effect was mentioned earlier (see page 13). Granger,⁹¹ Vanscheidt,⁹² and Martin⁹³ found that, in a room-temperature alkali-catalyzed reaction of a 1 to 1 mixture of phenol and formaldehyde, all the formaldehyde combined with approximately two-thirds of the phenol. *o*-Cresol and *p*-cresol behave similarly. The obvious conclusion, barring side reactions which were shown to be negligible, is that phenol polyalcohols are formed in an amount equivalent to the amount of unreacted phenol. Granger mentions that dilution of the reaction mixture tends to decrease polyalcohol formation. Even with 2 moles of formaldehyde per mole of phenol a considerable quantity of monoalcohols and some unreacted phenol are obtained.

Martin⁹⁴⁻⁹⁵ has found that the sodium salt of trimethylophenol can be precipitated by the addition of certain water-miscible organic solvents to a sodium phenate-formaldehyde reaction mixture without causing separation of the salts of the lower alcohols. Seto⁹⁶⁻⁹⁷ has also prepared such salts. Using Martin's technique, Goldblum⁵⁵ has measured the amount of trialcohol formed with various phenol-formaldehyde ratios. Goldblum's results, shown in Table II, p. 13, leave no doubt as to the strong tendency towards polyalcohol formation. Lewin and Robitschek⁹⁸ further indicate that commercial phenolics contain 10-20% free phenol. Smith, Rugg, and Bowman⁹⁹ found,

by infrared determination, between 2 and 15% unreacted phenol in typical phenolic resins. Vanscheidt⁸⁹ has shown how the amount of unreacted phenol varies with extent of reaction.

The formation of phenol polyalcohols, with the attendant quantity of unreacted phenol, explains why curing resins may be obtained by reaction under alkaline conditions of less than a mole of formaldehyde per mole of phenol.²⁷ During dehydration or the curing process the unreacted phenol is lost, leaving a residue having, in effect, more than a mole of combined formaldehyde per mole of phenol.

Polyalcohol formation even at low formaldehyde to phenol ratios is partly explained by statistical considerations and partly by the high reactivity of certain phenol alcohols toward formaldehyde.⁵⁸ The tendency towards polyalcohol formation also appears to be associated with the basicity of the catalyst employed, the stronger bases showing the greatest tendency towards polyalcohol formation.³⁸ This may be illustrated by the preparation of a series of resins using the same phenol-formaldehyde ratio but employing as catalysts progressively weaker bases such as NaOH, MgO, and ZnO. It will be noted that, upon dehydration of the resins, the amount of unreacted phenol is greatest where NaOH and least where the ZnO was the catalyst. The NaOH-catalyzed resins before dehydration will have the highest free phenol content and after dehydration will show the greatest thermosetting properties and will have the highest methylol content. The curing rate and methylol content of the resins will decrease roughly as the base strength of the catalyst. This principle finds wide application in the preparation of commercial resins.

PHENOL ALCOHOLS FROM PHENOL

The volume of literature available on the preparation and properties of phenol alcohols is so great as to preclude separate consideration of each phenol.^{3, 12, 20, 100} Instead, examples of the procedures followed and types of products obtained from each of the more important classes of phenols will be given, and references for a number of individual phenol alcohols will be found in Tables IV, V, and VI.

Of the numerous phenols commercially available the most important and most widely studied is phenol itself. Saligenin, the *ortho* monoalcohol of phenol, was one of the first phenol alcohols known, having been obtained by Piria¹⁰¹ in 1843 by hydrolysis of the natural glucoside salicin. This was nearly 30 years before Baeyer^{1, 102} began his studies of the reactions of phenols with aldehydes and more than 50 years before Lederer^{2, 103} and Manasse^{3, 104, 105} showed that the

compound could be prepared by the direct reaction of phenol with formaldehyde.

The method employed by Lederer involved the use of heat and a small amount of base, preferably sodium hydroxide or potassium hydroxide, whereas Manasse used molar quantities of base and carried out the reaction at room temperature. The latter procedure has now been generally adopted for the preparation of phenol alcohols except for phenols with strongly negative substituents, where alkaline catalysts are not applicable. The reason for the success of Manasse's procedure is now fairly well understood and involves several factors. Under alkaline conditions the addition of a methylol group is roughly proportional to catalyst concentration.^{8, 54, 106-108} Yet, above a minimum concentration a further increase in alkali has little or no increased effect on the rate of the resinification reactions.¹¹⁰⁻¹¹² Thus by going to a mole of caustic per mole of phenol a system highly favorable to the addition of methylol groups is obtained without appreciably increasing their tendency to resinify. As the resinification reaction has a large temperature coefficient, it is desirable to run the reaction at a low temperature, especially with highly reactive phenols.

According to Manasse, saligenin and *p*-hydroxybenzyl alcohol are prepared by dissolving 1 mole of phenol in a little more than 1 mole of 5% sodium hydroxide and reacting with 1 mole of formaldehyde at room temperature until the odor of formaldehyde has disappeared. The reaction mixture is then neutralized with dilute acetic acid, and the phenol alcohols and unchanged phenol are extracted with ether. After removal of the ether the phenol is removed by steam distillation, a mixture of saligenin and *p*-hydroxybenzyl alcohol being left. The phenol alcohols can be separated by extracting with hot benzene, which preferentially dissolves the *ortho* compound. The *para* compound is difficult to obtain pure by this method, and Ruderman¹¹³ recommends sublimation for purifying the compound. Koebner¹¹⁴ has described a procedure for preparing *o*- and *p*-hydroxybenzyl alcohol in improved yields. The improvement consists in using an excess of phenol, which minimizes the tendency towards polyalcohol formation.

Martin⁸¹ has described a procedure for separating mixtures of phenol alcohols. The phenol alcohols are prepared by Manasse's procedure. When the reaction is complete, water is removed from the reaction mixture under a vacuum at or near room temperature. The residue is then dissolved in several moles of pyridine and treated with trimethylchlorosilane. This treatment blocks the methylol and

phenolic hydroxyl groups with trimethylsilyl groups. Products of low viscosity and good thermal stability are obtained. The pyridine hydrochloride formed in the reaction is filtered off, and the trimethylsilyl derivatives are separated by fractional distillation. Hydrolysis of the trimethylsilyl derivatives, which occurs under neutral conditions, gives the free phenol alcohols. By the above procedure, *p*-hydroxybenzyl alcohol, 2,4-dimethylolphenol, and 2,4,6-trimethylolphenol were separated from a phenol-formaldehyde reaction mixture.

Reese ¹¹⁸ has succeeded in separating the polymethylol derivatives of phenol by extraction processes, and Freeman ⁸² and Reese ⁸¹ have achieved similar results chromatographically.

The sodium salt of trimethylolphenol was obtained by Martin by reacting approximately 3 moles of formaldehyde with 1 mole of sodium phenate at temperatures between 5° and 60°C.^{94,95} The salt was precipitated by pouring the reaction mixture into a suitable water-miscible organic solvent such as ethanol. The barium salt of trimethylolphenol was obtained in a similar manner. More recently Seto and Horiuchi ⁹⁶ have prepared the lithium salt of trimethylolphenol. This salt precipitates from the reaction mixture without the addition of a precipitating agent. By the addition of acid to a very dilute suspension of the sodium salt of trimethylolphenol Freeman ⁸⁴ and later Seto and Horiuchi ⁹⁶ obtained the free trimethylolphenol.

Carpenter and Hunter ⁸⁸ prepared trimethylolphenol by the reduction of the trimethyl ester of hydroxytrimesic acid with lithium aluminum hydride. Freeman ⁸⁴ also prepared trimethylolphenol as well as 2,4- and 2,6-dimethylolphenol by reduction of the methyl esters of hydroxytrimesic, 4-hydroxyisophthalic acid, and 2-hydroxyisophthalic acid respectively after acetylation of the phenolic hydroxyl groups. Kämmerer and Grossman ⁸⁸ used a somewhat different approach for the synthesis of saligenin and 2,4- and 2,6-dimethylolphenol. These authors started with *ortho* and *para* chlorinated phenols. The appropriate chlorophenols were reacted with formaldehyde, and the chlorine substituents were removed by reduction. By proper choice of the starting phenol, phenol alcohols having either one or two methylol groups located in preassigned positions could be prepared. Yields of purified phenol alcohols ran around 65%; crude yields ranged from 70% to 95%.

It is now well established that in addition to the mononuclear phenol alcohols tetramethyloldihydroxydiphenylmethanes are important products of the later stages of the reaction between phenol and formaldehyde. Walker ¹¹⁶ first reported the separation of 3,3',5,5'-tetramethylol-4,4'-dihydroxydiphenylmethane from a phenol-formaldehyde re-

action mixture in 1935. A few years later Seebach ¹¹⁷ made a detailed study of the compound and prepared a large number of its derivatives. Seebach reacted phenol with formaldehyde in the presence of magnesium oxide to obtain the compound. More recently Seto and Horiuchi ¹¹⁸ have used lithium, sodium, potassium, calcium, strontium, barium, and magnesium hydroxides as catalysts for the reaction. They found that the salts of the tetraalcohol crystallized from the reaction mixture in all cases except where calcium and potassium hydroxide were used. Sodium and barium hydroxide gave the highest yields of the tetraalcohol.

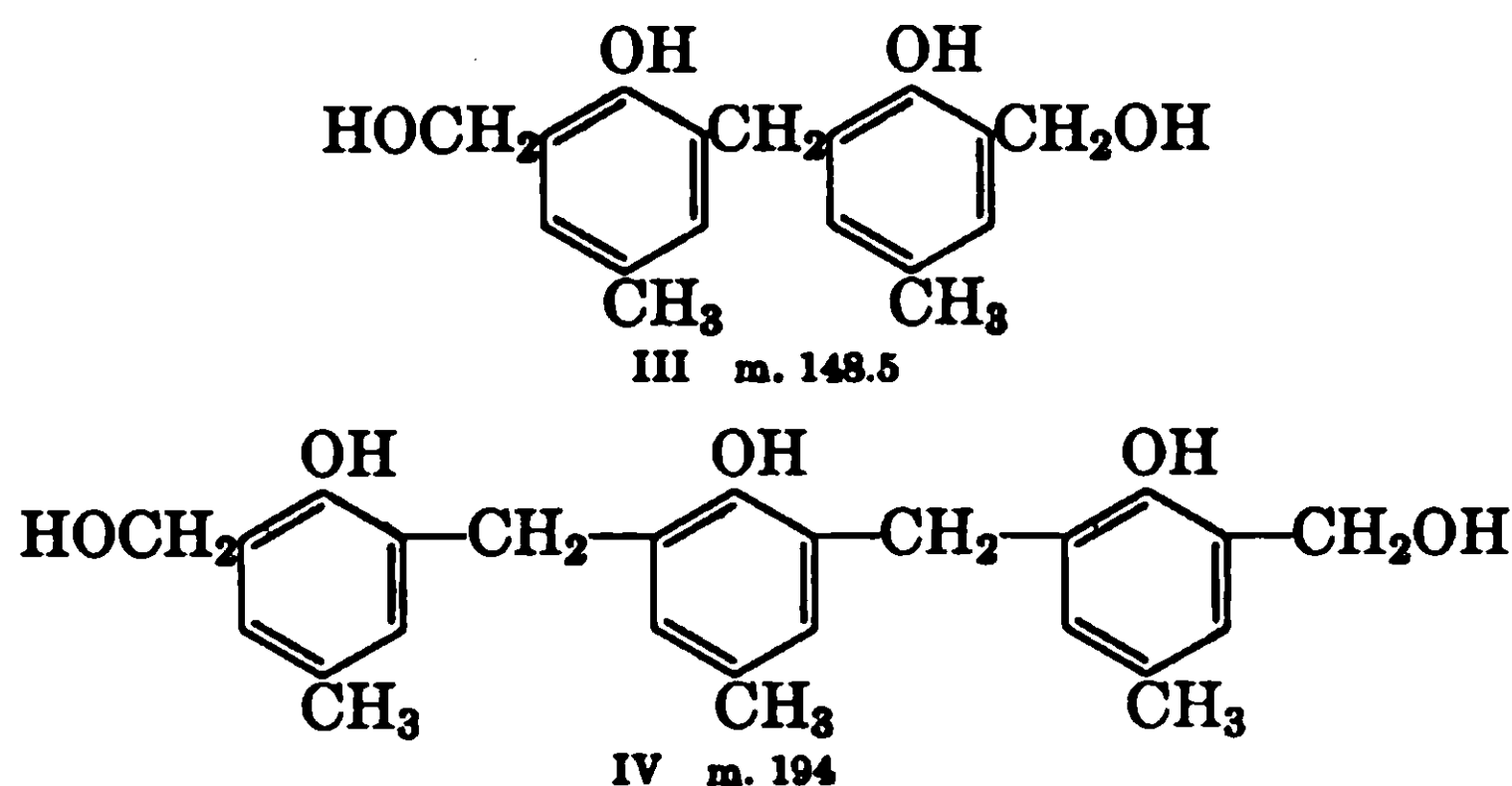
Seto ⁹⁷ has reported the synthesis of the tetramethylol derivatives of 2,2'- and 2,4'-dihydroxydiphenylmethane in addition to the previously known 4,4'-isomer. The tetramethylol derivative of 2,2'-dihydroxydiphenylmethane melts at 132–133°C., of the 2,4'-isomer at 117–118°C., and of the 4,4'-isomer at 145–146°C. Martin ⁹⁴ had previously obtained a compound melting at 130–132°C. which showed the correct analysis for a tetramethyloldihydroxydiphenylmethane. Although it was never proved, it would appear from the melting point that the compound obtained by Martin may have been the tetramethylol derivative of 2,2'-dihydroxydiphenylmethane.

Tetramethyloldihydroxydiphenylmethane is formed by the self-condensation of the salts of trimethylolphenol in aqueous solution. The reaction occurs by the elimination of water and formaldehyde between 2 moles of the trialcohol and appears to be a first-order reaction dependent on the concentration of trimethylolphenol.⁸⁸ This would mean that significant quantities of the tetraalcohol would be formed only in the later stages of a reaction between phenol and formaldehyde after appreciable quantities of the trialcohol had accumulated in the system. A high ratio of formaldehyde to phenol, e.g., in the neighborhood of 2 or 3 to 1, also favors the formation of the compounds, but they have been detected even at a ratio of 0.8 to 1.¹¹⁸ A long reaction period would favor the tetraalcohol; a somewhat shorter reaction period would give more of the trialcohol. Many of these points are well illustrated by the data presented by Freeman and Lewis ⁸⁸ (see pages 254–257).

Tetramethyloldihydroxydiphenylmethane also may be obtained from trimethylolphenol under acidic conditions.^{88, 80a, 84, 94} According to Reese,^{80a} benzyl ethers are obtained when trimethylolphenol is heated at 110°C. in the absence of a catalyst.

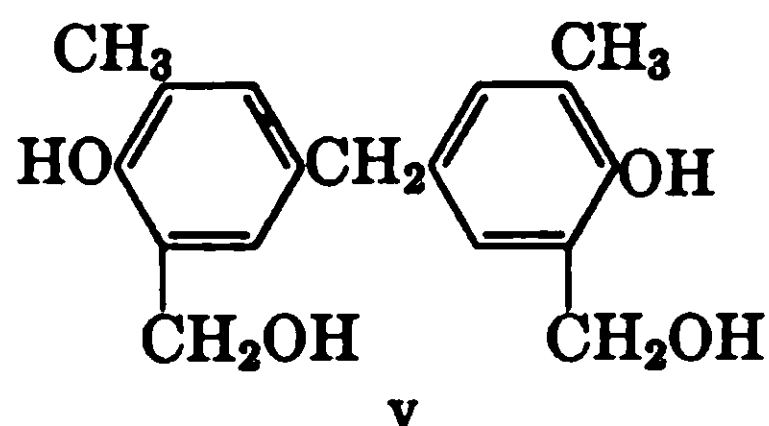
PHENOL ALCOHOLS FROM CRESOLS AND XYLENOLS

p-Cresol forms both a mono- and a dialcohol,^{2, 88, 118} and Auwers has described a procedure for separating the two alcohols.⁵⁹ Both Ullmann and Brittner¹¹⁹ and Auwers report excellent yields of the dialcohol by reaction of an alkaline solution of *p*-cresol with 2 moles of formaldehyde. If the caustic is sufficiently concentrated the dialcohol will precipitate from the reaction mixture as its sodium salt. Koebner¹²⁰ and Finn and Lewis¹²¹ have prepared the di- and trinuclear phenol alcohols, III and IV. The compounds were obtained by treat-



ing the di- and trinuclear phenols with formaldehyde in an alkaline solution.

o-Cresol is capable of forming both an *ortho* and a *para* monoalcohol as well as the *o,p*-dialcohol. The monoalcohols are somewhat difficult to prepare because of a tendency towards dialcohol formation, but both compounds have been obtained.^{2, 91, 122} Granger⁹¹ prepared the dialcohol as well as the dimethyloldihydroxyditolylmethane, V.



It is difficult to isolate the individual phenol alcohols of *m*-cresol. The difficulty may be attributed both to the large number of isomers (three monomethylol, three dimethylol, and one trimethylol derivative) and to the proneness of the compounds to resinify. Nevertheless, several crystalline derivatives have been reported,^{2, 8, 85, 123, 124} and

Reese¹²⁵ has succeeded in separating all of the seven possible *m*-cresol alcohols by chromatography. The sodium salt of trimethylol-*m*-cresol has been prepared and also a tetramethyloldihydroxyditolylmethane.^{91, 94, 95, 126}

Xylenols are a valuable source of phenol alcohols.^{112, 124, 126-129} Both 2,4- and 2,6-xylenol give monoalcohols, the latter compound showing a tendency to form a dihydroxydixylylmethane. 3,5-Xylenol is unique among the group in being trifunctional. Granger⁹¹ found that whereas 2 moles of formaldehyde are rapidly absorbed by this phenol the third mole of formaldehyde combines very sluggishly. Martin^{94, 95} also found this to be true and isolated the sodium salt of a dialcohol even when using 3 moles of formaldehyde per mole of 3,5-xylenol. The free dialcohol was readily obtained by acidification of the salt with dilute acetic acid. Auwers⁸⁹ apparently obtained the same compound in impure form. The location of the methylol groups was not established for the compound obtained by Martin. More recently Finn, Lewis, and Megson⁷⁰ and Kämmerer and Grossman⁸⁵ obtained a dialcohol in which the methylol groups were shown to be in the 2- and the 6-positions relative to the phenolic hydroxyl group. The difficulties in adding the third methylol group to 3,5-xylenol have been attributed to steric factors.⁹¹

PHENOL ALCOHOLS FROM MISCELLANEOUS PHENOLS

Phenol alcohols are readily obtained from the higher alkyl phenols, particularly when the substituents are located *ortho* or *para* to the phenolic hydroxyl group. The conditions used to obtain methylol derivatives of the cresols are in general applicable to the higher alkyl phenols, except that higher reaction temperatures may be required with phenols having long alkyl side chains. Organic solvents may also be necessary if the sodium salts of the substituted phenols are virtually insoluble in aqueous caustic.

The chlorinated phenols give phenol alcohols under conditions similar to those used with the alkyl phenols but may require longer reaction periods.^{180, 181} Chiddix and Williams¹⁸² have given a procedure for the preparation of phenol alcohols from phenols having one or more chlorine substituents. For 2,4,5-trichlorophenol they recommend the addition of the phenol, dissolved in an equivalent amount of caustic, to the required amount of 35% formalin at 45–50°C. The reaction mixture is stirred for 14 hours at 45–50°C., heated to 60°C. in 1 hour, and held at 60–65°C. for 2 hours. The yield is increased if the final reaction temperature was increased from 60–65° to 87–91°C.

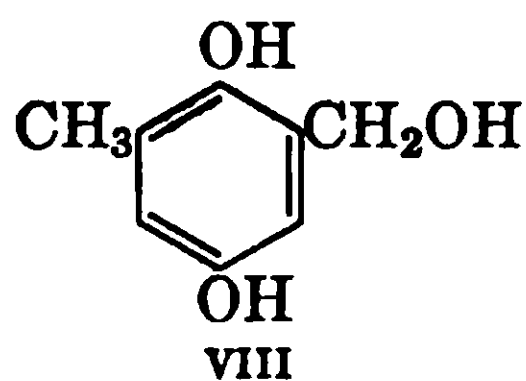
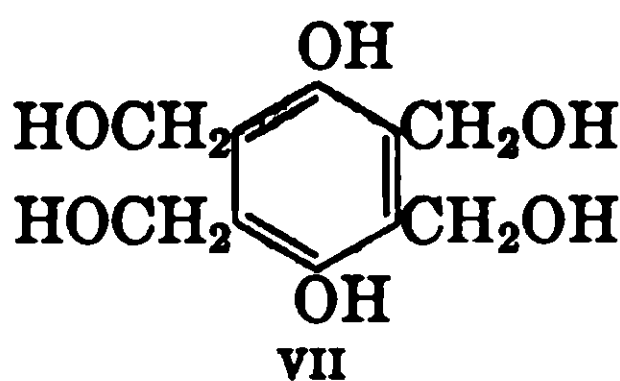
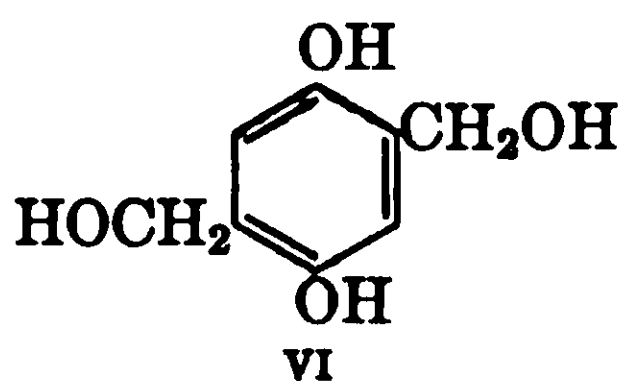
The nitrophenols are examples of phenols possessing strongly elec-

tronegative groups and hence require vigorous catalytic conditions if reaction with formaldehyde is to take place. Both of the *ortho* and *para* monoalcohols of *o*-nitrophenol have been prepared.^{133, 133} The compounds were obtained in one experiment by heating for 6 hours a mixture of 100 grams of *o*-nitrophenol, 160 grams of formalin, and 500 grams of concentrated hydrochloric acid. The crude product, 40 grams, was separated into two fractions by digesting the mixture with alcoholic potassium hydroxide, the *para* compound being soluble in the alkaline solution and the *ortho* compound being insoluble. Three parts of the *para* derivative were found for each part of the *ortho* compound. It is possible that the first products formed by reaction of the *o*-nitrophenol with the formalin in the presence of the hydrochloric acid were chloromethylphenols and that the phenol alcohols obtained resulted from the hydrolysis of the chloromethyl derivatives during the treatment with the alcoholic potassium hydroxide.

It has been reported that the monomethylol derivative of 6-methyl-2-nitrophenol can be prepared by the action of nitrous acid on 2,4-di(hydroxymethyl)-6-methylphenol.¹³⁴ 4-Nitrophenol forms only a single methylol derivative, which was isolated as an acetal.¹³⁵ 3-Nitrophenol has been reacted with formaldehyde but did not give a methylol derivative directly.^{136, 137}

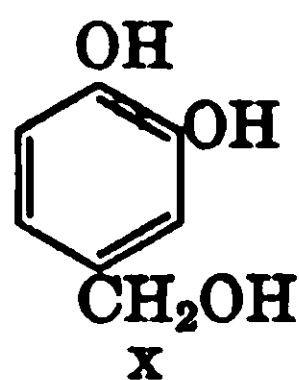
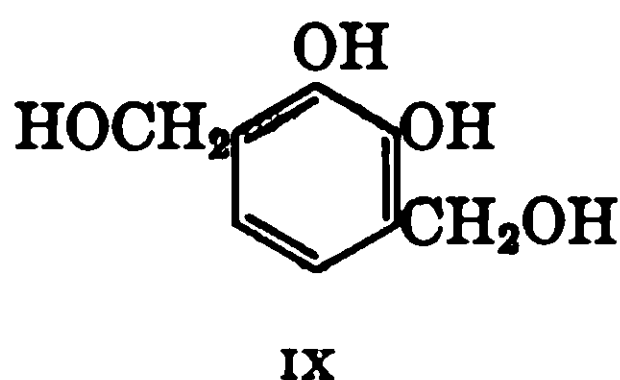
PHENOL ALCOHOLS FROM POLYHYDROXYPHENOLS

So far only monohydroxyphenols have been considered as sources of phenol alcohols. Several of the polyhydroxyphenols can be made to yield phenol alcohols. Hydroquinone reacts with formaldehyde and an alkaline catalyst to give the methylol derivatives VI and VII.¹³⁸⁻¹⁴⁰



Methyl hydroquinone forms the monoalcohol, VIII, according to Euler.¹⁴¹

As opposed to hydroquinone, catechol gave only a dialcohol, IX, on condensation with an excess of formaldehyde.¹³⁸ Rosenmund and

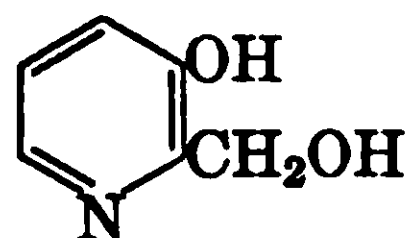
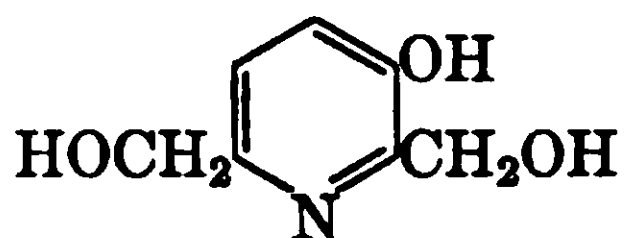
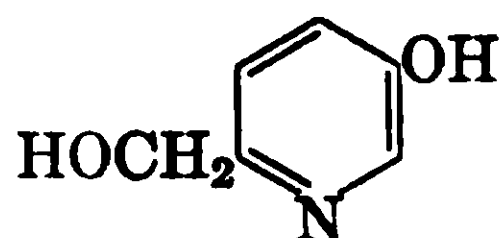


Boehm prepared the monomethylol derivative X by reduction of the corresponding aldehyde,¹⁴² but the compound has not been reported from the direct reaction of catechol with formaldehyde.

Resorcinol, because of the strong activation of two phenolic hydroxyl groups, is extremely reactive, and its methylol derivatives rapidly resinify. Boehm and Parlasca prepared methylol derivatives of resorcinol by reduction of the corresponding dicarbomethoxy aldehydes.¹⁴⁸ If the methylol group was *ortho* or *para* to the phenolic hydroxyl groups, the derivative always resinified; the compound with a *meta* methylol group was stable to acid. Sen and Sarkar claim to have prepared a monomethylol derivative of resorcinol by reaction in alkaline solution with formaldehyde at 0–5°C.¹⁴⁴ Since their product was insoluble in water, it is likely that the compound was partially resinified. Euler¹⁸⁸ obtained a dialcohol from resorcinol but did not establish its structure. Kyrning also obtained a methylol derivative of quinone.¹⁴⁰

Although α -naphthol reacts with formaldehyde to give products containing sufficient oxygen to indicate that phenol alcohols might be present, the alcohols have not been isolated in pure form. A methylol derivative of β -naphthol, m.p. 193 dec., has been reported.^{148, 146}

Of the three hydroxypyridines only the 3-hydroxy derivative shows typical phenolic character.¹⁴⁷ The last compound reacts with formaldehyde to give three methylol derivatives.^{148–150} The compounds were shown to have the following structures:



2-Hydroxy-3-hydroxymethyl-6-methylpyridine, m.p. 164–165, has been prepared indirectly.¹⁵¹ 2-Pyridone, in spite of its lack of phenolic character, reacts with formaldehyde to give 1-hydroxymethyl-2-pyridone, m.p. 86.¹⁵²

PHENOL ALCOHOLS FROM HIGHER ALDEHYDES OR KETONES

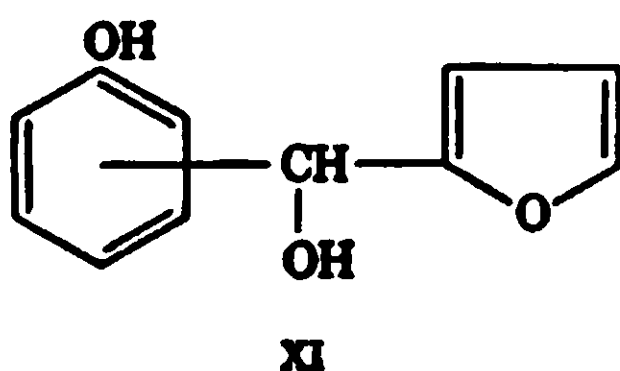
Higher aldehydes occasionally have been reacted with phenols to prepare phenol alcohols. However, their use has been seriously limited by the side reactions which occur when the aldehydes are brought into contact with the catalysts normally employed. Formaldehyde is relatively free of side reactions under acidic conditions, but it undergoes the Cannizzaro reaction under strongly alkaline conditions. This

competing reaction is not serious at room temperature even with a mole of caustic per mole of phenol. According to Carswell,²⁰ even at reflux temperature the reaction is virtually eliminated when the molar ratio of phenol to alkali is greater than 6 to 1. In contrast to formaldehyde, most of the higher aldehydes undergo side reactions such as the aldol type of condensation, this being particularly true under alkaline conditions. These side reactions which lead to self-resinification are very bothersome even in the presence of phenols.

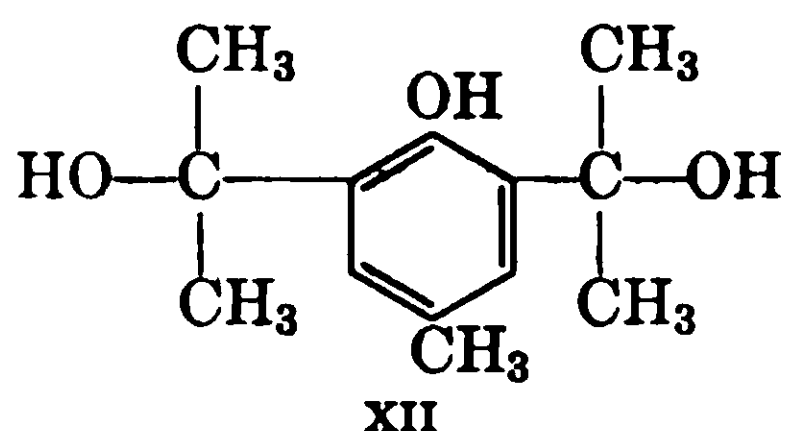
As might be anticipated the higher aldehydes which have been used with greatest success for the preparation of phenol alcohols have been those having no α hydrogens. Such aldehydes react in a manner analogous to formaldehyde. Of this group chloral has been studied most extensively, phenol alcohols having been prepared from it by reaction with phenols such as phenol, *p*-cresol, guiacol, catechol, resorcinol,¹⁵⁵ and 4-hydroxycoumarin.¹⁵⁴ The reactions were usually carried out at room temperature with potassium carbonate as catalyst, and in general the yields were good. Dharwarkar and Alimchandani¹⁵⁵ reacted salicylic acid with chloral in the presence of hydrogen chloride and obtained a product with a $(\text{CCl}_3)\text{CHCl}$ -group instead of a $(\text{CCl}_3)\text{CHOH}$ -group attached to the benzene ring.

Baeyer¹⁰⁵ was one of first workers to study the reactions of benzaldehyde with phenol. Although hydroxybenzhydrol was not obtained as a crystalline product by Baeyer it was postulated as an intermediate in the formation of the higher condensation products. Losev and Akutin¹⁵⁶ and Pope and Howard¹⁵⁷ have since obtained the compound in pure form. Pope and coworkers^{158,159} have also obtained a phenol alcohol by the reaction of benzaldehyde with 3-(dimethylamino)phenol. The formation of a phenol alcohol by the reaction of *p*-methylsalicylaldehyde and phenol has been reported. The same compound is obtained when *p*-cresol is reacted with *p*-hydroxybenzaldehyde.¹⁵⁰

By the very careful reaction of furfural with phenol a hydroxyphenylfurylcarbinol, XI, has been prepared, but the position of the substituted methylol group relative to the phenolic hydroxyl group has not been established.²⁶ It is interesting to note that the reaction was carried out under mildly acidic rather than under basic conditions.



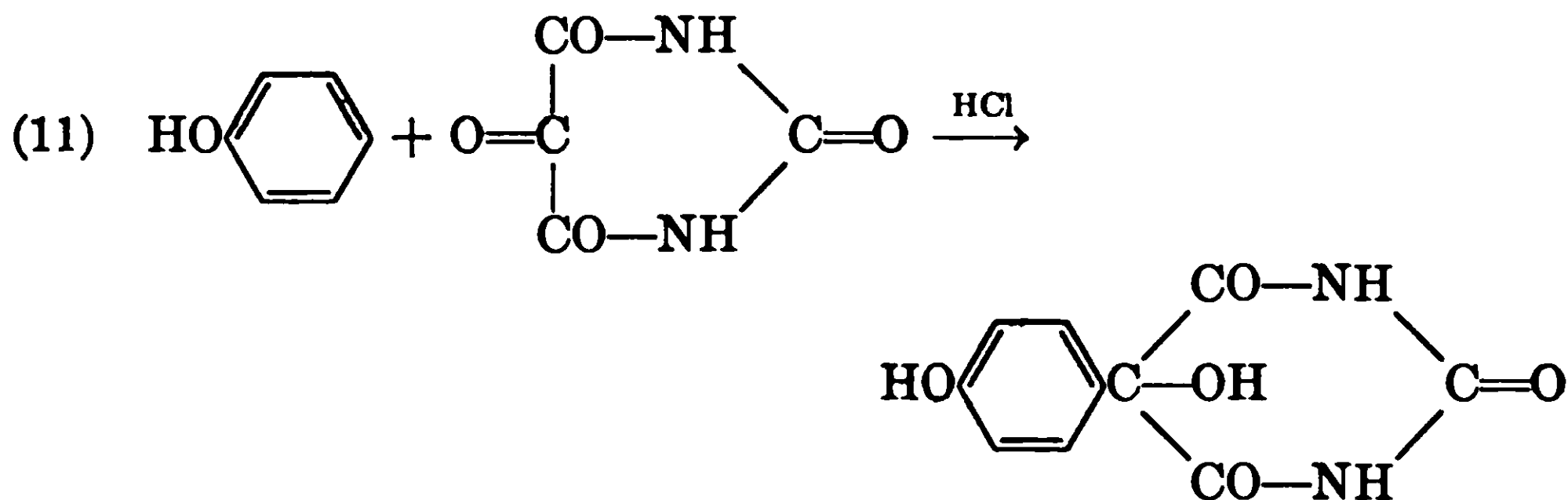
The most common reaction of unsubstituted dialkyl ketones with phenols is an acid-catalyzed reaction which results in the formation of dihydroxydiphenylalkanes (bisphenols). The strong tendency for phenol alcohols to condense under acidic conditions probably explains why the phenol alcohols which have been postulated as intermediates in the formation of dihydroxydiphenylalkanes have not been isolated. That certain of the phenol alcohols postulated as intermediates would be stable under neutral conditions has been shown by the indirect preparation of compounds such as the dialcohol, XII, which would be expected from the reaction of *p*-cresol with 2 moles of acetone if the reaction stopped at the phenol alcohol stage.¹⁶¹



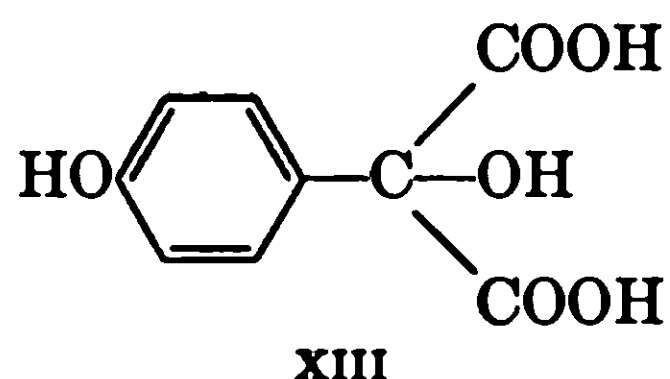
Under alkaline conditions, which normally favor phenol alcohol formation, dialkyl ketones are largely consumed by side reactions so that phenol alcohols are not obtained. Whereas the unsubstituted dialkyl ketones do not give phenol alcohols directly, compounds possessing polar groups adjacent to the keto group react with phenols to form stable phenol alcohols.¹⁶² Both acidic and basic catalysts have been employed for such reactions, the choice of catalyst depending on the keto compound used. Sodium glyoxylate, for example, condenses with guaiacol,^{162, 163} equation 10. Alloxan and phenol also react under



acidic conditions to form a complex type of phenol alcohol,^{162, 164, 165} equation 11. Acidic conditions were used for the condensation since

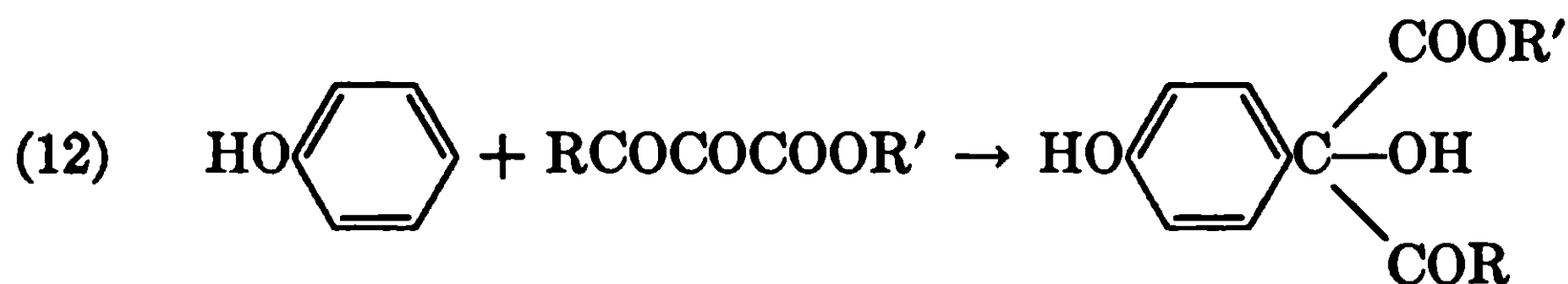


the cyclic derivative hydrolyzed under alkaline conditions to the hydroxymalonic acid, XIII. This compound may be viewed as a phenol

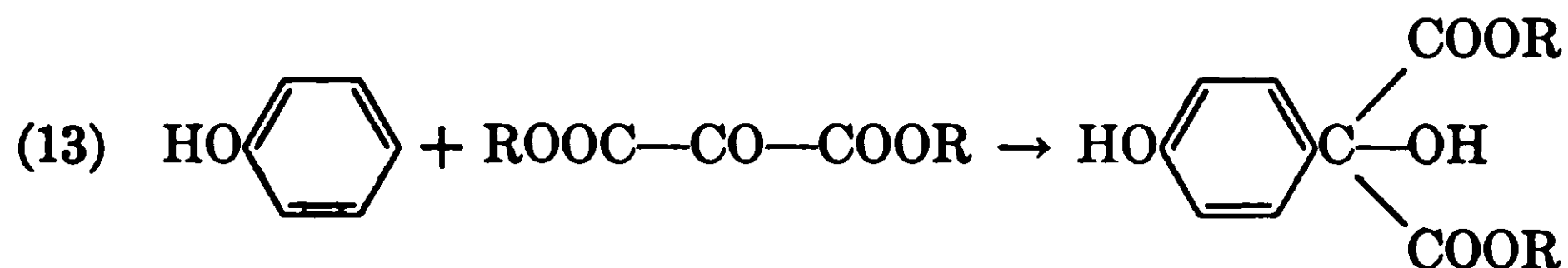


alcohol in which the hydrogens attached to the carbon atom of the methylol group have been replaced by carboxyl groups. Such compounds lose water and carbon monoxide when heated with acids to give hydroxyphenylglyoxylic acids.

α,β -Diketo esters condense with phenols in acetic acid, with anhydrous zinc chloride as catalyst, to give aldol-type condensation products in 75–85% yields,^{162,166} equation 12. Mesoxalates undergo a



similar reaction, equation 13. The products of this reaction are of



the same type as those obtained by hydrolysis of the alloxan-phenol condensation products. The fact that the above compounds are frequently prepared under acidic conditions illustrates how a methylol group can be stabilized by replacing the hydrogens on the carbon atom of the methylol group with negative groups.

In Tables IV, V, and VI are listed many of the phenol alcohols, together with their melting points and one or more pertinent references.

REFERENCES FOR CHAPTER 2

- ¹ A. Baeyer, *Ber.*, **5**, 25–20, 280–282, 1044–1100 (1872).
- ² L. Lederer, *J. prakt. Chem.*, (2), **50**, 223–226 (1894).
- ³ O. Manasse, *Ber.*, **27**, 2409–2413 (1894); U. S. pat. 526,786 (1894).
- ⁴ H. Stäger and J. Biert, *Helv. Chim. Acta*, **21**, 641–650 (1938).
- ⁵ C. C. Price, *Reactions at Carbon-Carbon Double Bonds*, Interscience Publishers, New York, 1946, p. 44.

Table IV. Mononuclear Phenol Alcohols

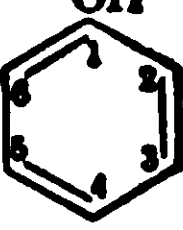
Parent Compound	Position of Substituents					M.P., °C.	References
	2	3	4	5	0		
	CH ₂ OH	85 86 86-87	2 4 167
	CH ₂ OH	73	171
	CH ₂ OH	111-112 126 124-125	3 89 168
	CH ₂ OH	CH ₂ OH	96 93-94 89 91.7-92.5 93	31 37 82 84 89
	CH ₂ OH	CH ₂ OH	101 96-98 94.7-96.2 98 101 101	31 79 84 85 115 169
	CH ₂ OH	CH ₂ OH	CH ₂ OH	84 75 91 76-78 79-82	37 82 115 170 197
	CH ₃	CH ₂ OH	81-84 105	122 172
	CH ₂	CH ₂ OH	40 32.8-83.8 39.6	2 91 169
	CH ₂	CH ₂ OH	CH ₂ OH	93 94 94	82 91 173
	CH ₂ OH	CH ₃	109	125
	CH ₃	CH ₂ OH	117 127	3 125
	CH ₂	CH ₂ OH	110 108 111	2 124 125
	CH ₂ OH	CH ₂	CH ₂ OH	132	125
	CH ₂ OH	CH ₂	CH ₂ OH	94 96	85 125
	CH ₂	CH ₂ OH	CH ₂ OH	118	125
	CH ₂ OH	CH ₃	CH ₂ OH	CH ₂ OH	137	125

Table IV. Mononuclear Phenol Alcohols (Continued)

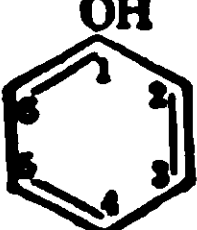

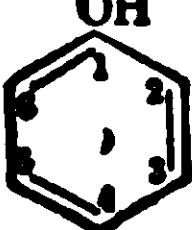
Parent Compound	Position of Substituents					M.P., °C.	References
	2	3	4	5	6		
	CH ₂ OH	CH ₃	195	3
						195	174
						196-197	175
	CH ₂ OH	CH ₃	CH ₂ OH	133-134	59
						128	113
						132	176
						129	177
	CH ₃	CH ₂ OH	CH ₃	174-175	59
						176	79
	CH ₂ OH	CH ₃	CH ₃	88	179
	CH ₂ OH	CH ₃	CH ₃	CH ₂ OH	147-148	79
						147	85
						147	169
	CH ₃	CH ₂ OH	CH ₃	176	112
						175	129
	CH ₃	CH ₂ OH	CH ₃	194-195	77
						194.5-195	127
	CH ₃	CH ₃	CH ₂ OH	57-58	194
						56	189
	CH ₃	CH ₃	CH ₂ OH	129
	CH ₂ OH	CH ₃	CH ₃	116	129
	CH ₂ OH	CH ₃	CH ₃	CH ₂ OH	111.5	128
						111.5-112.6	176
	CH ₂ OH	CH ₃	CH ₃	CH ₃	91-92	194
						91-92	181
	CH ₃	CH ₂ OH	CH ₃	CH ₃	130	178
						130	182
	C ₂ H ₅	CH ₂ OH	CH ₂ OH	86.5-87.5	184
						92-92.5	186
	CH ₂ OH	C ₂ H ₅	CH ₂ OH	84	113
						86-87	185
	<i>i</i> -C ₃ H ₇	CH ₂ OH	CH ₂ OH	89.6-90	186
	CH ₂ OH	<i>i</i> -C ₃ H ₇	CH ₂ OH	125	113
						125-127	176
						125-127	187
	CH ₂ OH	<i>n</i> -C ₃ H ₇	CH ₂ OH	88.5-89.5	184
						88-89	185
						84.5-85.8	188
	CH ₂ OH	<i>n</i> -C ₄ H ₉	CH ₂ OH	67-67.4	188
	CH ₂ OH	<i>sec</i> -C ₄ H ₉	CH ₂ OH	75.4-76.3	186

Table IV. Mononuclear Phenol Alcohols (Continued)

Parent Compound	Position of Substituents					M.P., °C.	References
	2	3	4	5	6		
OH 	<i>sec</i> -C ₄ H ₉	CH ₂ OH	CH ₂ OH	79-79.3	186
	CH ₂ OH	<i>t</i> -C ₄ H ₉	90-91	161 189
	CH ₂ OH	<i>t</i> -C ₄ H ₉	CH ₂ OH	61 and 75.5 74-75	177 176
	<i>t</i> -C ₄ H ₉	CH ₂ OH	CH ₂ OH	97-97.5 97-97.5	184 185
	CH ₂ OH	<i>t</i> -C ₄ H ₉	CH ₂ OH	48	190
	Cyclo-C ₆ H ₁₁	CH ₂ OH	CH ₂ OH	104-105	173
	CH ₂ OH	Cyclo-C ₆ H ₁₁	CH ₂ OH	107 107 106-107	113 188 190
	CH ₂ OH	C ₆ H ₅ CH ₂	CH ₂ OH	86	188
	CH ₂ OH	(CH ₂) ₂ CCH ₂ -C(CH ₂) ₂ -	CH ₂ OH	71 73.5 70	113 177 191
	<i>n</i> -C ₁₅ H ₃₁	CH ₂ OH	60-80	69
	<i>i</i> -C ₃ H ₇	CH ₂ OH *	CH ₂	120-121	3
	<i>i</i> -C ₃ H ₇	CH ₂	CH ₂ OH	86	2
	CH ₂	<i>t</i> -C ₃ H ₉	CH ₂ OH	64 63 and 74	192 193
	CH ₂	CH ₂ OH	<i>t</i> -C ₄ H ₉	96-97	104
	<i>t</i> -C ₄ H ₉	CH ₂	CH ₂ OH	Oil	194
	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	CH ₂ OH	98-99	25
	CH ₃	Cyclo-C ₆ H ₁₁	CH ₂ OH	78	192
	CH ₂ OH	C ₆ H ₅	CH ₂ OH	110-112 113-114 110-111.5	177 187 190
	OCH ₂	CH ₂ OH	115	3
	OCH ₂	CH ₂ OH	CH ₂ OH	104.5-106 105-106	173 218
	CH ₂ OH	OCH ₂	CH ₂ OH	128 126-127 127-128	173 219 220

* Location of methylol group uncertain.

Table IV. Mononuclear Phenol Alcohols (Continued)

Parent Compound	Position of Substituents					M.P., °C.	References
	2	3	4	5	6		
	OCH ₃	CH ₂ CH=CH ₂	CH ₂ OH	37 37-38	2 104
	CH ₂ OH	OH	CH ₂ OH	190-191 190-191 190-191	140 183 197
	CH ₂ OH	CH ₂ OH	OH	CH ₂ OH	CH ₂ OH	212-213 208-209 208-209	138 140 197
	OH	CH ₂ OH	CH ₂ OH *	116-117 116 116	138 140 197
	CH ₂ OH	OH	CH ₃	156.5-157.5	141
	CHO	CH ₂ OH	108	195
	CHO	CH ₂ OH	CH ₂ OH	119-121	197
	CHO	CH ₂ OH	CH ₃	83	195
	CH ₂ OH	CHO	CHO	129-130	197
	Cl	CH ₂ OH	123 122-123 and 127 123.5-124.5	195 196 198
	Cl	CH ₂ OH	116 115	190 203
	Cl	CH ₂ OH	CH ₂ OH	117.5-119 117.5-119	173 198
	CH ₂ OH	Cl	93	199
	CH ₂ OH	Cl	CH ₂ OH	154-155 164 153-154 165	131 176 187 202
	CH ₂ OH	CH ₃	Cl	CH ₂ OH	131 125.5-126.5 135-136	113 176 187
	CH ₃	Cl	CH ₂ OH	61	202
	CH ₂ OH	CH ₃	Cl	CH ₃	CH ₂ OH	183 dec. 166	176 205
	CH ₂ OH	Cl	COOH	165.5-166	204
	CH ₂ OH	CH ₃	Cl	<i>t</i> -C ₄ H ₉	62-64	206

* Location of methylol group uncertain.

Table IV. Mononuclear Phenol Alcohols (Continued)

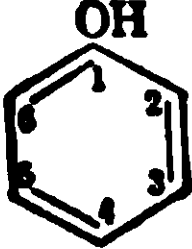
Parent Compound	Position of Substituents					M.P., °C.	Refer- ences
	2	3	4	5	6		
	Cl	Cl	CH ₂ OH	80-81	196
						82	200
						83	201
						70	202
	Cl	CH ₂ OH	Cl	86	199
	CH ₂ OH	Cl	Cl	Cl	CH ₂ OH	149 dec.	184
						146-147	185
						146-147	187
	CH ₂ OH	Cl	Cl	Cl	123-124	132
	CH ₂ OH	Cl	F		243
	CH ₂ OH	CF ₃	66-66.5	242
	CH ₂ OH	Br	109	199
							207
	CH ₂ OH	Br	CH ₂ OH	160 dec.	202
	Br	CH ₃	CH ₂ OH	35-36	212
	CH ₂ OH	Br	Br	87-88	199
						81-82 (crude)	209
						86	210
	Br	CH ₂ OH	Br		208
	CH ₃	Br	CH ₂ OH	Br	CH ₃	190	211
	CH ₃	Br	CH ₂ OH	CH ₃	Br	166	216
	Br	Br	CH ₂ OH	CH ₃	Br	174-176	214
						170-180 dec.	215
	Br	CH ₂ Br	CH ₂ OH	Br	CH ₂ OH	153	213
	Br	Br	CH ₂ OH	Br	CH ₂ OH	145-146	217
	Br	Br	CH ₂ OH	CH ₂ OH	Br	185	215
	Br	Br	CH ₂ OH	C ₆ H ₅ NHCH ₃ —	Br	171	215
	Br	Br	CH ₂ OH	CH ₂ Br	Br	166-167	215
	Br	CH ₂ Br	Br	Br	CH ₂ OH	142-143	213
	Br	Br	CH ₂ OH	CH ₂ I	Br	193	215
	NO ₂	CH ₂ OH	97	68
						97	195
						97	222
						97	223
	NO ₂	CH ₂ OH	75	68
	CH ₂ OH	NO ₂	126	225
	NO ₂	...	CH ₂ OH	CH ₃	95	124

Table IV. Mononuclear Phenol Alcohols (Continued)

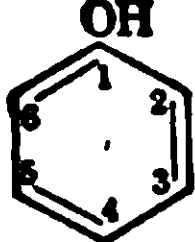
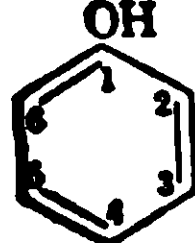
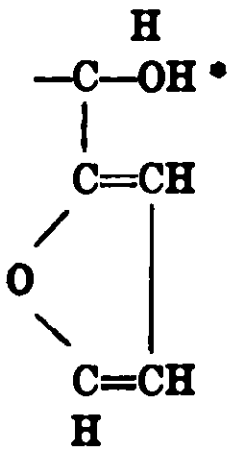

Parent Compound	Position of Substituents					M.P., °C.	References
	2	3	4	5	6		
	NO ₂	CH ₃	CH ₂ OH	98	134
	CH ₂ OH	NH ₂	232
	CH ₂ OH	NO ₂ C ₆ H ₄ N ₂ —	163	234
	CH ₂ OH	C ₆ H ₅ N ₂ —	CH ₃	96 96	226 229
	CH ₂ OH	CH ₃	C ₆ H ₅ N ₂ —	118-119 117.6	227 228
	CH ₂ OH	CH ₃	CH ₃	C ₆ H ₅ N ₂ —	147	128
	CH ₂ OH	C ₆ H ₅ N ₂ —	OCH ₃	122-124	226
	CH ₂ OH	COOH	>270	230
	CH ₂ OH	COOH	142	230
	CH ₂ OH	CH ₃	—CHSCN	86	233

Table V. Phenol Alcohols from Higher Aldehydes and Ketones

Parent Compound	Position of Substituents					M.P., °C.	References
	2	3	4	5	6		
	—CH(CCl ₃)OH	87	153
	—CH(CCl ₃)OH	CH ₃	147.5 147-148	16 153
	OCH ₃	—CH(CCl ₃)OH	118-119	163
	OH	—CH(CCl ₃)OH	176	153
	OH	—CH(CCl ₃)OH	128-129	153
		~150	26
	—CH(C ₆ H ₅)OH	200 dec.	157 235
	—CH(C ₆ H ₅)OH	—N(CH ₃) ₂	146	158
	—CH(p-HOC ₆ H ₄)OH	CH ₃	183-184	160
	—C(CH ₃) ₂ OH	OH	138	224
	—C(CH ₃) ₂ OH	CH ₃	—C(CH ₃) ₂ OH	110.5-111.5	184

* Location of methylol group uncertain.

Table VI. Dinuclear Phenol Alcohols

Parent Compound	Position of Substituents										M.P., °C.	Refer- ences
	2	3	4	5	6	2'	3'	4'	5'	6'		
	OH	CH ₂ OH	OH	135 132.5-134	32 241
	OH	CH ₂ OH	OH	121 121.5-123	32 241
	OH	CH ₂ OH	CH ₂ OH	OH	122-123	170
	OH	CH ₂ OH	OH	CH ₂ OH	126-127	241
	OH	CH ₂ OH	OH	155.5 155-158	32 170
	OH	CH ₂ OH	OH	112.5	32
	OH	CH ₂ OH	OH	108.5 106-108	32 241
	CH ₂ OH	OH	OH	130 124-126	32 241
	CH ₂ OH	OH	CH ₂ OH	OH	174 173	32 241
	CH ₂ OH	OH	CH ₂ OH	CH ₂ OH	OH	CH ₂ OH	145	116
	OH	CH ₂ OH	CH ₂ OH	OH	CH ₂ OH	CH ₂ OH	132-133	97

OH	CH ₂ OH	CH ₂ OH	CH ₂ OH	OH	CH ₂ OH	117-118	97
....	CH ₂ OH	OH	OH	CH ₃	111-112	241
OH	CH ₂ OH	CH ₃	OH	CH ₃	148 136-136.5 148	129 238 240
....	CH ₂ OH	OH	CH ₃	CH ₂ OH	OH	CH ₃	155 155	91 190
OH	CH ₂ OH	CH ₃	OH	CH ₂ OH	CH ₃	147-148 146-147.5 144 151-151.5	185 231 236 238
CH ₃	CH ₂ OH	OH	CH ₂ OH	CH ₃	CH ₂ OH	OH	CH ₂ OH	172	125
OH	CH ₂ OH	CH ₃	CH ₃	OH	CH ₂ OH	CH ₃	CH ₃	147	128
OH	CH ₂ OH	CH ₃	CH ₃	OH	CH ₂ OH	CH ₃	CH ₃	170 d.	237
....	OCH ₃	OH	CH ₂ OH	OCH ₃	OH	CH ₂ OH	148-149 149-150	183 239
OH	CH ₂ OH	Cl	OH	Cl	165-167	131
OH	CH ₂ OH	Cl	OH	CH ₂ OH	Cl	147-148	296
....	CH ₂ OH	OH	Cl	CH ₂ OH	OH	Cl	141	190
OH	CH ₂ OH	CH ₂ OH	OH	Br	Br	141-142	170
OH	CH ₂ OH	Br	OH	CH ₂ OH	Br	149-151 dec.	241

- ⁶ J. I. De Jong and J. De Jonge, *Rec. trav. chim.*, **72**, 497 (1953).
- ⁷ K. Hultsch, *Angew. Chem.*, **A60**, 179-184 (1948).
- ⁸ K. Hultsch, *Chemie der Phenolhärze*, Springer-Verlag, Berlin, 1950.
- ⁹ D. C. Pepper, *Chemistry & Industry*, 1941, 866.
- ¹⁰ P. D. Caesar and A. N. Sachanen, *Ind. Eng. Chem.*, **40**, 922-928 (1948).
- ¹¹ Von Joh F. Ehlers, *Kolloid-Z.*, **190**, Pt. 3, 161-165 (1953).
- ¹² J. F. Walker, *Formaldehyde*, Reinhold Publishing Corp., New York, 1944, pp. 162-189; 2nd Ed., 1953, pp. 235-271.
- ¹³ H. L. Bender, private communication.
- ¹⁴ J. Breslauer and J. Pictet, *Ber.*, **40**, 3785 (1907).
- ¹⁵ A. Reyckler, *Bull. soc. chim. France*, **I**, 1195 (1907).
- ¹⁶ M. P. Balfe and W. C. Webber, *J. Chem. Soc.*, 1942, 718.
- ¹⁷ F. D. Chattaway and A. A. Morris, *J. Chem. Soc.*, 1927, 2013-2017.
- ¹⁸ F. D. Chattaway, *J. Chem. Soc.*, 1926, 2720-2727.
- ¹⁹ F. D. Chattaway and F. Calvert, *J. Chem. Soc.*, 1927, 685.
- ²⁰ T. S. Carswell, *Phenoplasts*, Interscience Publishers, New York, 1947, pp. 6-54.
- ²¹ L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, **17**, 225-237 (1925).
- ²² L. Claisen, *Ber.*, **19**, 3316 (1886); *Ann.*, **257**, 270 (1887); *Z. angew. Chem.*, **56**, 478 (1923).
- ²³ H. von Euler and S. V. Kispeczy, *Z. physik. Chem.*, **A189**, 109 (1941).
- ²⁴ R. Wegler, *Angew. Chem.*, **60**, 88 (1948).
- ²⁵ R. Wegler and K. Faber, *Chem. Ber.*, **82**, 327 (1949).
- ²⁶ A. Porai-Koschutz, N. Kudryanzeff, and B. Maschkileison, *Kunststoffe*, **23**, 97-100 (1933).
- ²⁷ L. H. Baekeland, *J. Ind. Eng. Chem.*, **4**, 737-743 (1912).
- ²⁸ E. Ziegler and I. Simmler, *Ber.*, **74B**, 1871-1879 (1941).
- ²⁹ J. Scheiber and R. Barthel, *J. prakt. Chem.*, **147**, 99-109 (1936).
- ³⁰ R. Wegler and E. Regel, *Makromolekulare Chem.*, **9**, 1 (1952).
- ³¹ J. Reese, *Angew. Chem.*, **66**, 170-173 (1954).
- ³² S. R. Finn, J. W. James, and C. J. S. Standen, *Chemistry & Industry*, Feb. 13, 1954, p. 188.
- ³³ J. H. Freeman, private communication.
- ³⁴ H. S. Lilley, *J. Soc. Chem. Ind.*, **67**, 196-199 (1948).
- ³⁵ E. G. K. Pritchett, *Chemistry & Industry*, 1949, 295-299.
- ³⁶ K. Hultsch, *Kunst.*, **37**, 57-63 (1949); **39**, 192 (1949).
- ³⁷ R. W. Martin, *J. Am. Chem. Soc.*, **74**, 4208 (1952).
- ³⁸ I. W. Ruderman, *J. Soc. Chem. Ind.*, **64**, No. 7, 204 (1945).
- ³⁹ H. A. Bruson, U. S. pat. 2,114,122 (1938).
- ⁴⁰ H. A. Bruson, *J. Am. Chem. Soc.*, **58**, 1741 (1936).
- ⁴¹ W. J. Burke, *J. Am. Chem. Soc.*, **71**, 609 (1949).
- ⁴² W. J. Burke, R. P. Smith, and C. Weatherbee, *J. Am. Chem. Soc.*, **74**, 602 (1952).
- ⁴³ W. J. Burke and C. W. Stephens, *J. Am. Chem. Soc.*, **74**, 1518 (1952).
- ⁴⁴ W. J. Burke, M. J. Kolbezen, and C. W. Stephens, *J. Am. Chem. Soc.*, **74**, 3601 (1952).
- ⁴⁵ R. Bell, private communication.
- ⁴⁶ H. Moschatos and B. Tollens, *Ann.*, **272**, 271 (1842); M. Harvey and L. H. Barkeland, *Ind. Eng. Chem.*, **13**, 135 (1921).
- ⁴⁷ A. Zinke and St. Pucher, *Monatsh.*, **79**, 26-41 (1948).

- ⁴⁸ A. Zinke, G. Zigeuner, G. Weiss, and W. Leupold-Löwenthal, *Monatsh.*, **81**, 1098-1107 (1950).
- ⁴⁹ A. Zinke, G. Zigeuner, and G. Weiss, *Monatsh.*, **80**, 148-150 (1949).
- ⁵⁰ A. Zinke, G. Zigeuner, G. Weiss, and E. Wiesenberger, *Monatsh.*, **80**, 160-109 (1949).
- ⁵¹ G. Zigeuner, W. Schaden, and O. Gabriel, *Monatsh.*, **81**, 1108-1112 (1950).
- ⁵² A. Zinke, F. Hanus, and H. Pichelmayer, *Monatsh.*, **78**, 311-316 (1948).
- ⁵³ A. Zinke, G. Zigeuner, G. Weiss, and W. Schaden, *Monatsh.*, **81**, 999-1006 (1950).
- ⁵⁴ M. M. Sprung, *J. Am. Chem. Soc.*, **63**, 334-343 (1941).
- ⁵⁵ K. B. Goldblum, private communication.
- ⁵⁶ S. R. Finn and G. J. Lewis, *J. Applied Chem.*, **1**, 1-12, 560-562 (1951).
- ⁵⁷ G. R. Sprengling and C. W. Lewis, Preprint *Bull., Div. Paint, Varnish, and Plastics Chem.*, American Chemical Society Meeting, September, 1952, p. 77; *J. Am. Chem. Soc.*, **75**, 5709 (1953).
- ⁵⁸ J. H. Freeman and C. W. Lewis, Preprint *Bull., Div. Polymer Chem.*, American Chemical Society Meeting, September, 1953, p. 2S; *J. Am. Chem. Soc.*, **76**, 2080-2087 (1954).
- ⁵⁹ K. Auwers, *Ber.*, **40**, 2524-2537 (1907).
- ⁶⁰ G. R. Sprengling and J. H. Freeman, *J. Am. Chem. Soc.*, **72**, 1982-1985 (1950).
- ⁶¹ K. H. Meyer, *Trans. Faraday Soc.*, **82**, 345 (1936).
- ⁶² R. W. Martin, "Alkali-Catalyzed Phenol-formaldehyde Reaction," American Chemical Society Meeting, Springfield, Mass., December, 1948.
- ⁶³ W. T. Caldwell and T. R. Thompson, *J. Am. Chem. Soc.*, **61**, 765-767 (1939); **61**, 2354 (1939).
- ⁶⁴ J. C. Duff, *J. Chem. Soc.*, 1941, 547.
- ⁶⁵ R. C. Carlin and H. P. Landerl, *J. Am. Chem. Soc.*, **72**, 2762-2763 (1950).
- ⁶⁶ R. C. Carlin, *J. Am. Chem. Soc.*, **67**, 928 (1945).
- ⁶⁷ S. Seto, in press.
- ⁶⁸ J. B. Fishman, *J. Am. Chem. Soc.*, **42**, 2288-2297 (1920).
- ⁶⁹ E. R. H. Jones and I. K. M. Robson, Brit. pat. 634,960 (1950).
- ⁷⁰ S. R. Finn, G. J. Lewis, and N. J. L. Megson, *J. Soc. Chem. Ind.*, **69**, 129-132 (1950).
- ⁷¹ K. Auwers, *Ann.*, **856**, 124,148 (1907).
- ⁷² J. I. De Jong and J. De Jonge, *Rec. trav. chim.*, **71**, 643-660, 661-667 (1952).
- ⁷³ K. Hultsch, *Angew. Chem.*, **61**, 93-96 (1949).
- ⁷⁴ W. Huckel, *Theoretische Grundlagen der organische chemie*, Becker and Erler, Leipzig, 1943, p. 281.
- ⁷⁵ R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, **78**, 1260-1269 (1947).
- ⁷⁶ C. Eberhardt and Ad. Welter, *Ber.*, **27**, 1804-1814 (1895).
- ⁷⁷ E. Adler, H. von Euler, and J. D. Cedwall, *Arkiv Kemi Mineral. Geol.*, **A15**, No. 7, 1-17 (1941).
- ⁷⁸ K. Hultsch, *Ber.*, **74**, 1533-1534, 1534-1543 (1941).
- ⁷⁹ H. L. Bender, H. G. Farnham, J. W. Guyer, F. N. Apel, and T. B. Gibb, Jr., Preprint *Bull., Div. Paint, Varnish and Plastics Chem.*, American Chemical Society Meeting, September, 1950, pp. 73-77.
- ⁸⁰ H. L. Bender, A. G. Farnham, J. W. Guyer, F. N. Apel, and T. B. Gibb, Jr., *Ind. Eng. Chem.*, **44**, 1619 (1952).
- ^{80a} J. Reese, *Kunststoffe*, **45**, 137-145 (1955).

- ⁸¹ R. W. Martin, *J. Am. Chem. Soc.*, **74**, 3024-3025 (1952).
- ⁸² J. H. Freeman, *Anal. Chem.*, **24**, 2001 (1952); **24**, 955 (1952).
- ⁸³ A. T. Carpenter and R. F. Hunter, *Plastics*, 1950, 287; *J. Applied Chem.*, **1**, Pt. 5, 217-226 (1951).
- ⁸⁴ J. H. Freeman, *J. Am. Chem. Soc.*, **74**, 6257 (1952).
- ⁸⁵ H. Kämmerer and M. Grossman, *Ber.*, **86**, 1492-1494 (1953).
- ⁸⁶ A. A. J. Sigtermans, *Polytech. Tijdschr.*, **5**, 370a-372a (1950).
- ⁸⁷ G. E. Little and K. W. Pepper, *Brit. Plastics*, **19**, 430 (1947).
- ⁸⁸ Aero Research, Ltd., Oxford, England, *Sci. and Tech. Memo.*, December, 1946, pp. 1-47.
- ⁸⁹ A. A. Vanscheidt and A. A. Vasiliev, *J. Applied Chem. U.S.S.R.*, **19**, 7 (1946).
- ⁹⁰ M. Koebner, *Brit. Plastics*, **14**, 95-101 (1942).
- ⁹¹ F. S. Granger, *Ind. Eng. Chem.*, **24**, 442-447 (1932).
- ⁹² A. Vanscheidt, *Org. Chem. Ind. U.S.S.R.*, **3**, 385-393 (1937).
- ⁹³ R. W. Martin, unpublished results.
- ⁹⁴ R. W. Martin, *J. Am. Chem. Soc.*, **73**, 3952-3954 (1951).
- ⁹⁵ R. W. Martin, U. S. pat. 2,579,329 (1951).
- ⁹⁶ S. Seto and H. Horiuchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (6), **56**, 419-420 (1953).
- ⁹⁷ S. Seto et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (6), **56**, 890-892 (1953).
- ⁹⁸ A. Lewin and P. Robitschek, *Brit. Plastics*, 316-322; 385-391 (1945).
- ⁹⁹ J. J. Smith, F. N. Rugg, and H. N. Bowman, *Anal. Chem.*, **24**, 497 (1952).
- ¹⁰⁰ C. Ellis, *The Chemistry of Synthetic Resins*, Reinhold Publishing Corp., New York, 1935, pp. 277-454.
- ¹⁰¹ R. Piria, *Ann.*, **43**, 75 (1843).
- ¹⁰² A. Baeyer, *Ber.*, **5**, 280, 1094 (1872).
- ¹⁰³ L. Lederer, U. S. pat. 563,975 (1896).
- ¹⁰⁴ O. Manasse, *Ber.*, **35**, 3846 (1902).
- ¹⁰⁵ O. Manasse, U. S. pat. 526,786 (1894).
- ¹⁰⁶ R. Dubrisay, *Inds. plastiques*, **1**, No. 5, 132 (1945).
- ¹⁰⁷ A. A. Vanscheidt and R. I. Gruz, *J. Applied Chem. U.S.S.R.*, **21**, 502-511 (1948).
- ¹⁰⁸ T. T. Jones, *J. Soc. Chem. Ind.*, **65**, No. 9, 264-275 (1946).
- ¹⁰⁹ L. M. Debing, G. E. Murray, and R. J. Schatz, *Ind. Eng. Chem.*, **44**, 356-359 (1952).
- ¹¹⁰ F. S. Granger, *Ind. Eng. Chem.*, **29**, 860, 1125 (1937).
- ¹¹¹ K. B. Goldblum, Preprint *Bull., Div. Paint, Varnish and Plastics Chem.*, American Chemical Society Meeting, September, 1950, pp. 60-67.
- ¹¹² E. L. Holmes and N. J. L. Megson, *J. Soc. Chem. Ind.*, **52**, 415-418T (1933).
- ¹¹³ I. W. Ruderman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 753-759 (1946).
- ¹¹⁴ M. Koebner, Brit pat. 558,987 (1944).
- ¹¹⁵ J. Reese, *Angew. Chem.*, **64**, 399-400 (1952).
- ¹¹⁶ E. E. Walker, *Trans. Faraday Soc.*, **32**, 345 (1935).
- ¹¹⁷ F. Seebach, *Ber.*, **72B**, 1635 (1939); **73**, 1338 (1940).
- ¹¹⁸ S. Seto and H. Horiuchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (5), **56**, 354-355 (1953).
- ¹¹⁹ F. Ullmann and K. Brittner, *Ber.*, **42**, 2539-2548 (1909).
- ¹²⁰ M. Koebner, *Z. angew. Chem.*, **46**, 251-256 (1933).
- ¹²¹ S. R. Finn and G. J. Lewis, *J. Soc. Chem. Ind.*, **69**, 132-133 (1950).
- ¹²² F. Hanus, *J. prakt. Chem.*, N.F. **155**, 317-331 (1940).

- 123 Bayer and Co., German pat. 85,588 (1844).
- 134 N. J. L. Megson and A. A. Drummond, *J. Soc. Chem. Ind.*, 49, 251-257T (1930).
- 123 J. Reese, *Chem. Ber.*, 86, 979-985 (1953).
- 139 F. S. Granger, *Ind. Eng. Chem.*, 29, 1305-1308 (1937).
- 127 E. Bamberger, *Ber.*, 86, 2028 (1903).
- 123 E. Ziegler, G. Zigeuner, and A. Kainzner, *Monatsh.*, 80, 295-302 (1949).
- 129 K. Auwers and O. Anselmino, *Ber.*, 35, 137-144 (1902).
- 130 R. W. Martin, *Anal. Chem.*, 23, 883-884 (1951).
- 131 H. E. Faith, *J. Am. Chem. Soc.*, 72, 837-839 (1950).
- 132 M. E. Chiddix and M. R. Williams, U. S. pat. 2,631,169 (1953).
- 133 J. B. Fishman, *J. Am. Chem. Soc.*, 42, 2297-2302 (1920).
- 134 E. Ziegler and K. Gartler, *Monatsh.*, 80, 634-639 (1949).
- 133 W. Borsche and A. D. Berkhout, *Ann.*, 830, 82 (1904).
- 136 D. R. Mehta and P. R. Ayyar, *J. Univ. Bombay*, 8, Pt. 3, 176-183 (1939).
- 137 C. A. Buehler, F. Deebel, and R. Evans, *J. Org. Chem.*, 6, 216-219 (1941).
- 133 H. von Euler, E. Adler, and G. J. Gie, *Arkiv Kemi Mineral. Geol.*, B14, No. 9, 1-7 (1940).
- 139 H. von Euler, E. Adler, S. de Kispoczy, and A. Fagerlund, *Arkiv Kemi Mineral. Geol.*, A14, No. 10, 1-20 (1940).
- 140 S. Kyrning, *Arkiv Kemi Mineral. Geol.*, B15, No. 11, 1-8 (1940).
- 141 H. von Euler, E. Adler, and A. O. Caspersson, *Arkiv Kemi Mineral. Geol.*, A16, No. 11, 1-14 (1943).
- 142 K. W. Rosenmund and T. Boehm, *Arch. Pharm.*, 264, 448-459 (1926).
- 143 T. Boehm and H. Parlasca, *Arch. Pharm.*, 270, 168-182 (1932).
- 144 R. W. Sen and N. N. Sarkar, *J. Am. Chem. Soc.*, 47, 1084-1085 (1925).
- 146 C. M. Suter, R. K. Bair, and F. G. Bordwell, *J. Org. Chem.*, 10, 470-478 (1945).
- 146 P. W. Clutterbuck and J. B. Cohen, *J. Chem. Soc.*, 1923, 2507-2515.
- 147 R. C. Elderfield, *Heterocyclic Compounds*, Vol. I, John Wiley & Sons, New York, 1950, pp. 442 and 531.
- 143 T. Urbanski, *J. Chem. Soc.*, 1946, 1104.
- 149 T. Urbanski, *Przemysl Chem.*, 26, 193-200 (1947).
- 130 A. Stempel and E. C. Buzzi, *J. Am. Chem. Soc.*, 71, 2969-2971 (1949).
- 151 R. P. Mariella and A. J. Havlik, *J. Am. Chem. Soc.*, 74, 1915 (1952).
- 152 Swiss pat. 243,101 (1946).
- 133 H. Pauly and A. Schantz, *Ber.*, 56, 979 (1923).
- 134 M. Ikawa and K. P. Link, *J. Am. Chem. Soc.*, 72, 4373-4374 (1950).
- 133 H. V. Dharwarkar and R. L. Alimchandani, *J. Indian Chem. Soc.*, 17, 416-421 (1940).
- 136 I. P. Losev and M. S. Akutin, *J. Applied Chem. U.S.S.R.*, 18, 916-925 (1940).
- 157 F. G. Pope and H. Howard, *J. Chem. Soc.*, 97, 78 (1910).
- 133 S. Krishna and F. G. Pope, *J. Chem. Soc.*, 119, 286 (1921).
- 139 F. G. Pope and H. Howard, *Angew. Chem.*, (9), 18, 49 (1922).
- 130 J. E. Driver and J. B. Sousa, *J. Chem. Soc.*, 1954, 985-989.
- 161 S. van der Meer, *Rubber Chem. and Technol.*, 18, 853-873 (1945).
- 132 L. N. Ferguson, *Chem. Revs.*, 88, 231 (1946).
- 163 G. C. Helintzer and B. Rodnevich, *J. Applied Chem. U.S.S.R.*, 8, 909 (1935).
- 134 J. Schwyzer, *Chem. Ztg.*, 54, 817, 839 (1930).
- 163 C. F. Bohringer and Sohne, Ger. pats. 107,720 and 115,817 (1901).

- 166 A. Gugyot and A. Gry, *Bull. soc. chim. France*, (4), 7, 902 (1910).
- 167 A. Lapworth and J. B. Shoesmith, *J. Chem. Soc.*, 121, Pt. 2, 1396 (1922).
- 168 R. Mozingo and K. Folkers, *J. Am. Chem. Soc.*, 70, 229 (1948).
- 169 S. R. Finn and J. W. G. Musty, *J. Applied Chem.*, 2, 88-90 (1952).
- 170 A. T. Carpenter and R. F. Hunter, *J. Applied Chem.*, 1, Pt. 5, 217-226 (1951).
- 171 G. Lock, *Ber.*, 62, 1177 (1929).
- 172 C. Schotten, *Ber.*, 11, 788 (1878).
- 173 F. Hanus, *J. prakt. Chem.*, (2), 158, 245-253 (1941).
- 174 N. J. L. Megson and W. A. Wood, *Nature*, 140, 642-643 (1937).
- 175 H. von Euler, E. Adler, G. Eklund, and O. Torngren, *Arkiv Kemi Mineral. Geol.*, B15, No. 9, 1-7 (1942).
- 176 R. W. Martin, "Condensation of Methylol Anisoles," presented Division Polymer Chemistry, American Chemical Society Meeting, September, 1952, Atlantic City.
- 177 W. Charlton and L. E. Perrins, *J. Oil & Colour Chemists' Assoc.*, 30, No. 324, 185 (1947).
- 178 S. R. Finn, N. J. L. Megson, and E. J. W. Whittaker, *Chemistry & Industry*, S849-853 (1950).
- 179 S. R. Finn and J. W. G. Musty, *J. Applied Chem.*, 1, 782-784 (1951).
- 180 H. von Euler, E. Adler, and J. O. Cedwall, *Arkiv Kemi Mineral. Geol.*, A14, No. 14A, 1-20 (1941).
- 181 T. Zincke and C. von Hohorst, *Ann.*, 353, 357-379 (1907).
- 182 S. R. Finn and J. W. G. Musty, *J. Soc. Chem. Ind.*, Suppl. Issue, No. 1, S3-7 (1950).
- 183 H. von Euler, E. Adler, and D. Friedman, *Arkiv Kemi Mineral. Geol.*, B13, No. 12, 1-7 (1939).
- 184 J. Strating and H. J. Backer, *Rec. trav. chim.*, 62, 57 (1943).
- 185 S. van der Meer, Paper 47, *Rubber Stichting*, Delft, Holland, 1944.
- 186 I. W. Ruderman, *J. Am. Chem. Soc.*, 70, 1662-1663 (1948).
- 187 S. van der Meer, *Rec. trav. chim.*, 63, 147-156 (1944).
- 188 F. Hanus and E. Fuchs, *J. prakt. Chem.*, (2), 152, 327-336 (1939).
- 189 S. van der Meer, *Rec. trav. chim.*, 63, 157-169 (1944).
- 190 A. Zincke, E. Hanus, and E. Ziegler, *J. prakt. Chem.*, (2), 152, 126-144 (1939).
- 191 J. B. Niederl, *Ind. Eng. Chem.*, 30, 1269 (1938).
- 192 K. Hultzs, *J. prakt. Chem.*, 158, 275-294 (1941).
- 193 G. Sprengling, S. Beatty, and K. B. Adams, *J. Am. Chem. Soc.*, 72, 4314 (1950).
- 194 K. Hultzs, *J. prakt. Chem.*, 159, 155-179 (1941).
- 195 R. Stoermer and K. Behn, *Ber.*, 34, 2455-2460 (1901).
- 196 C. A. Buehler, R. L. Brown, J. M. Holbert, F. G. Fulmer, and G. W. Parker, *J. Org. Chem.*, 6, 902-907 (1941).
- 197 A. T. Carpenter and R. F. Hunter, *J. Chem. Soc.*, 1954, 2731.
- 198 F. Hanus, *J. prakt. Chem.*, 158, 254-265 (1941).
- 199 C. Mettler, *Ber.*, 39, 2933-2942 (1906).
- 200 K. Hultzs, *Ber.*, 75B, 106-114 (1942).
- 201 B. Dunning, *Chem. Zentr.*, I, 335 (1937).
- 202 M. Weiler and K. Berres, German pat. 510,447 (1929).
- 203 A. Reissert and K. Crämer, *Ber.*, 61, 2565 (1928).
- 204 C. A. Buehler, B. C. Bass, R. B. Darling, and M. E. Lubs, *J. Am. Chem. Soc.*, 62, 890 (1940).

- ²⁰² S. R. Finn and G. J. Lewis, *J. Applied Chem.*, **1**, Pt. 11, 524-526 (1951).
- ²⁰⁶ H. E. Faith, U. S. pat. 2,560,760 (1951).
- ²⁰⁷ K. Auwers, *Ann. Chem.*, **302**, 138 (1898).
- ²⁰⁸ K. Auwers and S. Daecke, *Ber.*, **33**, 3379 (1900).
- ²⁰⁹ A. T. Carpenter and R. F. Hunter, *J. Applied Chem.*, **1**, Pt. 5, 217-226 (1951).
- ²¹⁰ E. Ziegler, H. Meralla, and I. Simmler, *Ber.*, **76**, 664-669 (1943).
- ²¹¹ K. Auwers and K. Traun, *Ber.*, **32**, 3309 (1899).
- ²¹² E. Adler, S. Tingstam, and A. O. Caspersson, *Arkiv Kemi Mineral. Geol.*, **B15**, No. 10, 1-8 (1942).
- ²¹³ O. Anselmino, *Ber.*, **35**, 144-150 (1902).
- ²¹⁴ K. Auwers and E. Ziegler, *Ber.*, **29**, 2348-2355 (1896.)
- ²¹⁶ K. Auwers and R. V. Erggelet, *Ber.*, **32**, 3016-3033 (1899).
- ²¹⁶ K. Auwers and F. Baum, *Ber.*, **29**, 2338-2348 (1896).
- ²¹⁷ K. Auwers and W. Hampe, *Ber.*, **32**, 3005-3016 (1899).
- ²¹⁸ G. Goethals, *Natuurw. Tijdsch. Nederland*, **18**, 247-255 (1936).
- ²¹⁸ L. Helfer, *Helv. Chim. Acta*, **7**, 955 (1924).
- ²²⁰ W. J. Moran, E. C. Schreiber, E. Engel, D. C. Behn, and J. L. Yamins, *J. Am. Chem. Soc.*, **74**, 127 (1952).
- ²²¹ H. von Euler, E. Adler, and B. Bergstrom, *Arkiv Kemi Mineral. Geol.*, **B14**, No. 25, 1-6 (1941).
- ²²² K. Fries and G. Fickenworth, *Ber.*, **41**, 367 (1908).
- ²²² M. C. Hart and A. D. Hirschfelder, *J. Am. Chem. Soc.*, **42**, 2678-2686 (1920).
- ²²⁴ A. Bell and D. J. Shields, U. S. pat. 2,639,288 (1953).
- ²²² H. Einhorn, *Ann.*, **343**, 244-245 (1905).
- ²²² G. Zigeuner and E. Ziegler, *Monatsh.*, **79**, 89 (1948).
- ²²⁷ E. Marder and I. W. Ruderman, *J. Am. Chem. Soc.*, **73**, 5475-5476 (1951).
- ²²² E. Ziegler and G. Zigeuner, *Monatsh.*, **79**, 42-54 (1948).
- ²²² E. Ziegler and G. Zigeuner, *Monatsh.*, **79**, 363-370 (1948).
- ²²⁰ H. Reimer, *Ber.*, **11**, 790 (1878).
- ²²¹ R. F. Hunter, R. A. Morton, and A. T. Carpenter (in part), *J. Chem. Soc.*, **1950**, 441-444.
- ²²² Bayer and Co., German pat. 148,977.
- ²²² E. Ziegler and H. Lüdde, *Monatsh.*, **79**, 316-322 (1948).
- ²²⁴ E. Ziegler and G. Zigeuner, *Monatsh.*, **79**, 358-362 (1948).
- ²²² G. Zigeuner and E. Ziegler, *Monatsh.*, **80**, 359-363 (1949).
- ²²² H. Zinke, F. Hanus, H. Prennschütz-Schützenau, and H. Troger, *Ber.*, **74B**, 206-214 (1941).
- ²²⁷ G. Zigeuner, E. Ziegler, W. Schaden, and W. Weisenberger, *Monatsh.*, **81**, 326-329 (1950).
- ²²² E. Adler, *Arkiv Kemi Mineral. Geol.*, **B14**, No. 23, 1-7 (1941).
- ²²² E. Adler and S. Kyrning, *Svensk Kem. Tid.*, **53**, No. 1, 5-11 (1940).
- ²⁴⁰ P. Maitland and O. C. Pepper, *J. Soc. Chem. Ind.*, **61**, 66 (1942).
- ²⁴¹ A. T. Carpenter and R. F. Hunter, *J. Applied Chem.*, **3**, Pt. 11, 486-495 (1953).
- ²⁴² M. Hauptschein, C. S. Stokes, and A. J. Saggiomo, *J. Am. Chem. Soc.*, **76**, 4476-4477 (1954).
- ²⁴² J. D. Head, U. S. pat. 2,639,298 (1953).

C H A P T E R T H R E E

Dihydroxydiphenylalkanes

Excluding the resinous condensation products, the dihydroxydiphenylalkanes are the largest-volume phenol-aldehyde or phenol-ketone products in commercial use. These materials, which are often referred to as bisphenols, find use as antioxidants,¹⁻¹² germicidal, bactericidal, or teniacidal agents,^{10, 13-23} pharmaceuticals,²⁴⁻³⁰ surface-active agents,^{31, 32} fungicides,³³ pesticides,^{34, 35} and for the preparation of synthetic tannins and ion-exchange resins.^{36, 37} In addition the compounds may be used to increase the functionality of oil-soluble resins.^{38, 39} They also may be reacted with epichlorohydrin and caustic to give polyepoxide resins which are used in pottings, castings, adhesives, surface coatings, and as stabilizers for polyvinyl chloride and other chlorinated polymers.⁴⁰⁻⁴²

Dihydroxydiphenylmethanes were probably first prepared by the reduction of selected dihydroxydiphenyl ketones. They were also prepared very early by the direct reaction of phenols with formalin under acidic conditions. Reaction under acidic conditions, sometimes referred to as the Baeyer reaction, remains the most important means for preparing dihydroxydiphenylalkanes and is the only practical method where the higher aldehydes and ketones are used. The methods available for the preparation of dihydroxydiphenylalkanes are listed below:

1. Acid-catalyzed condensation of phenols with aldehydes and ketones.
2. Base-catalyzed reaction of phenols with aldehydes and ketones (limited mainly to formaldehyde).
3. Condensation of phenol alcohols or other hydroxybenzyl compounds with phenols.
4. Self-condensation of phenol alcohols.
5. Loss of formaldehyde from dihydroxydibenzyl ethers.
6. Rearrangement of diphenylacetals.

7. Reaction of acetylenes with phenols.
8. Reduction of selected ketones.
9. Reaction of dihalogen compounds with phenols.

Strictly speaking, the last four methods do not belong in a discussion of phenol-aldehyde chemistry. They have been included in the listing above for the sake of completeness. There is obviously some overlapping in the first six procedures.

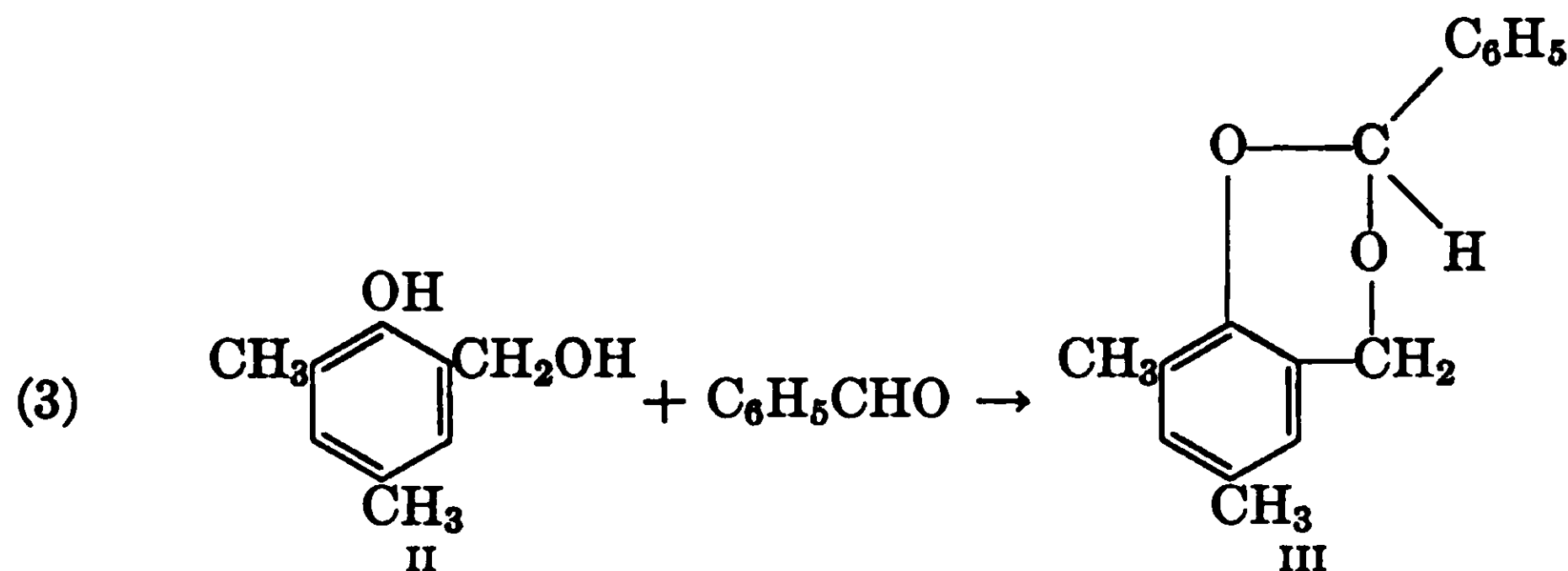
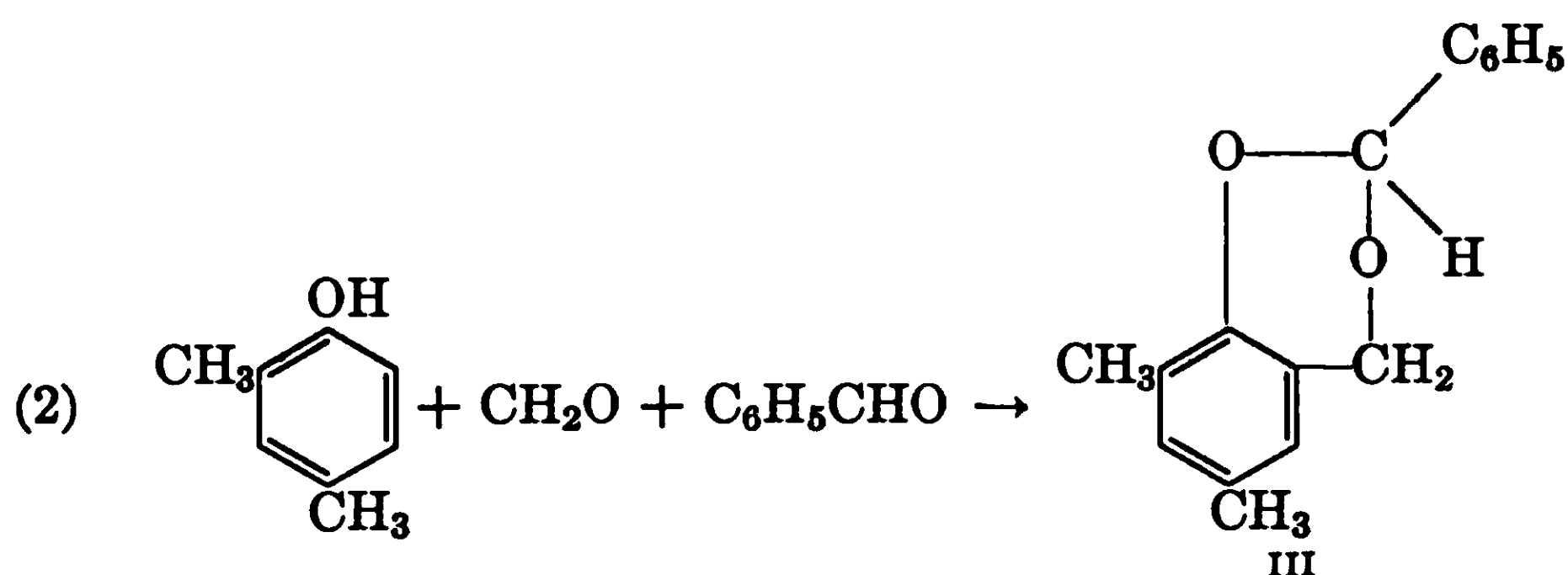
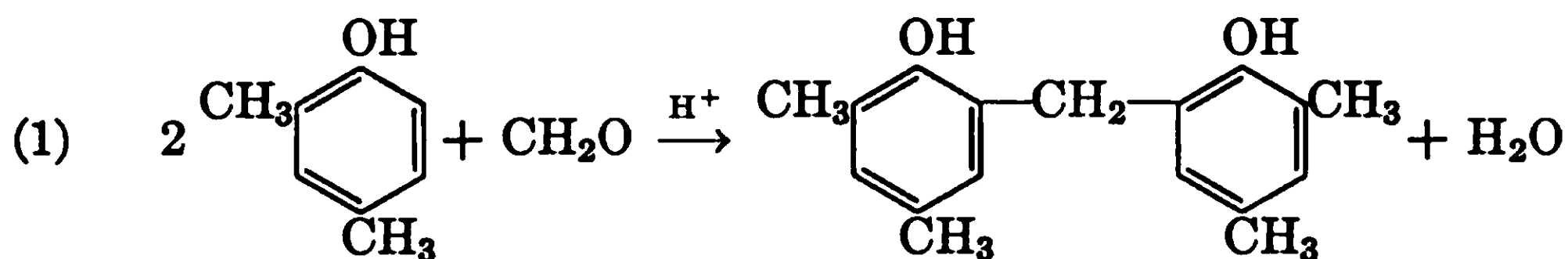
ACID-CATALYZED CONDENSATION

Baeyer⁴³ established the general nature of the condensation of aldehydes and ketones with phenols under acidic conditions. During these studies benzaldehyde was reacted with phenol and a polynuclear product was obtained. Baeyer thought that this product resulted from the condensation of a hydroxybenzhydrol with additional phenol.⁴⁴ This was probably the first expression of the theory that phenol alcohols are intermediates in the formation of dihydroxydiphenylalkanes. The theory now finds wide acceptance.⁴⁵⁻⁵⁵

One of the most convincing arguments in support of the theory is the isolation of phenol alcohols during the early stages of the reaction. Phenol alcohols may be obtained, even in the presence of moderate concentrations of acid, by the reaction of formaldehyde with phenols having negative substituents.^{56, 57} The phenol alcohols from the more reactive phenols and cresols are sufficiently sensitive to acids that their isolation is difficult in the presence of acidic materials, but even here phenol alcohols also have been found.^{58-55, 58} Low reaction temperature, a dilute reaction medium, and low concentration of acid all help to preserve the phenol alcohols. Bender⁵⁷ reports that many phenol alcohols become sensitive to traces of strong acids above approximately 20°C. By means of chromatography Finn and coworkers^{58a} and Reese^{60a, 59b} have succeeded in separating the whole scale of phenol alcohols, including the trialcohol, from a phenol-formaldehyde reaction mixture where hydrochloric acid was used as catalyst. Freeman^{60a} has obtained *o*- and *p*-hydroxybenzyl alcohol from a reaction mixture where sulfuric acid was used as a catalyst. Traces of phenol alcohols have also been recovered from typical novolac preparations.

Some of the higher aldehydes and ketones such as chloral,⁵⁹ furfural,⁶⁰ benzaldehyde,⁶¹ acetophenone,⁶² certain of the keto acids and esters, and alloxan⁶³⁻⁶⁵ give phenol alcohols when condensed with phenols under acidic conditions.

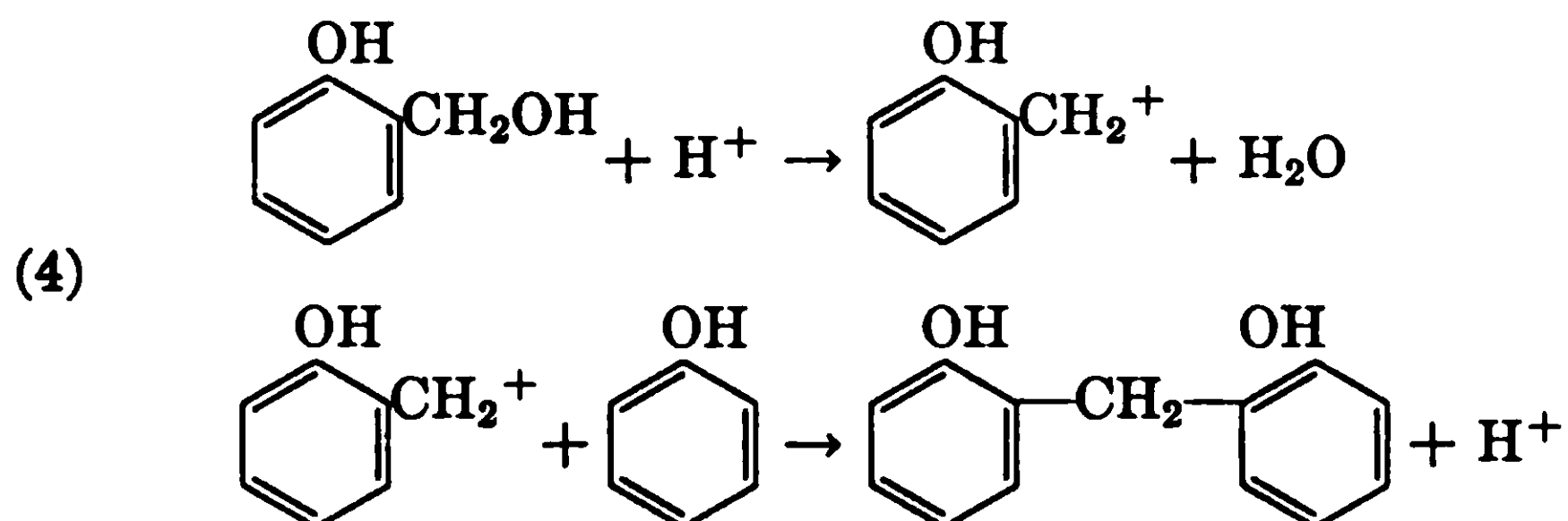
The formation of phenol alcohols under acidic conditions is also supported by the results obtained when certain reagents are added to a phenol-formaldehyde reaction mixture.⁶⁶ In such cases the same product is formed by the joint reaction of the added reagent with the phenol and the aldehyde as is obtained by the direct reaction of the reagent with the phenol alcohol anticipated as an intermediate but prepared by an independent method. The result of such an experiment is summarized in equations 1, 2, and 3. The added reagent in this



example is benzaldehyde. As shown in equation 1 the reaction of 2,4-dimethylphenol with formaldehyde results in the formation of a methylene derivative. With benzaldehyde present along with the phenol and formaldehyde a benzodioxan, III, results, reaction 2. The benzodioxan also is obtained by the direct reaction of benzaldehyde with the phenol alcohol II, reaction 3.

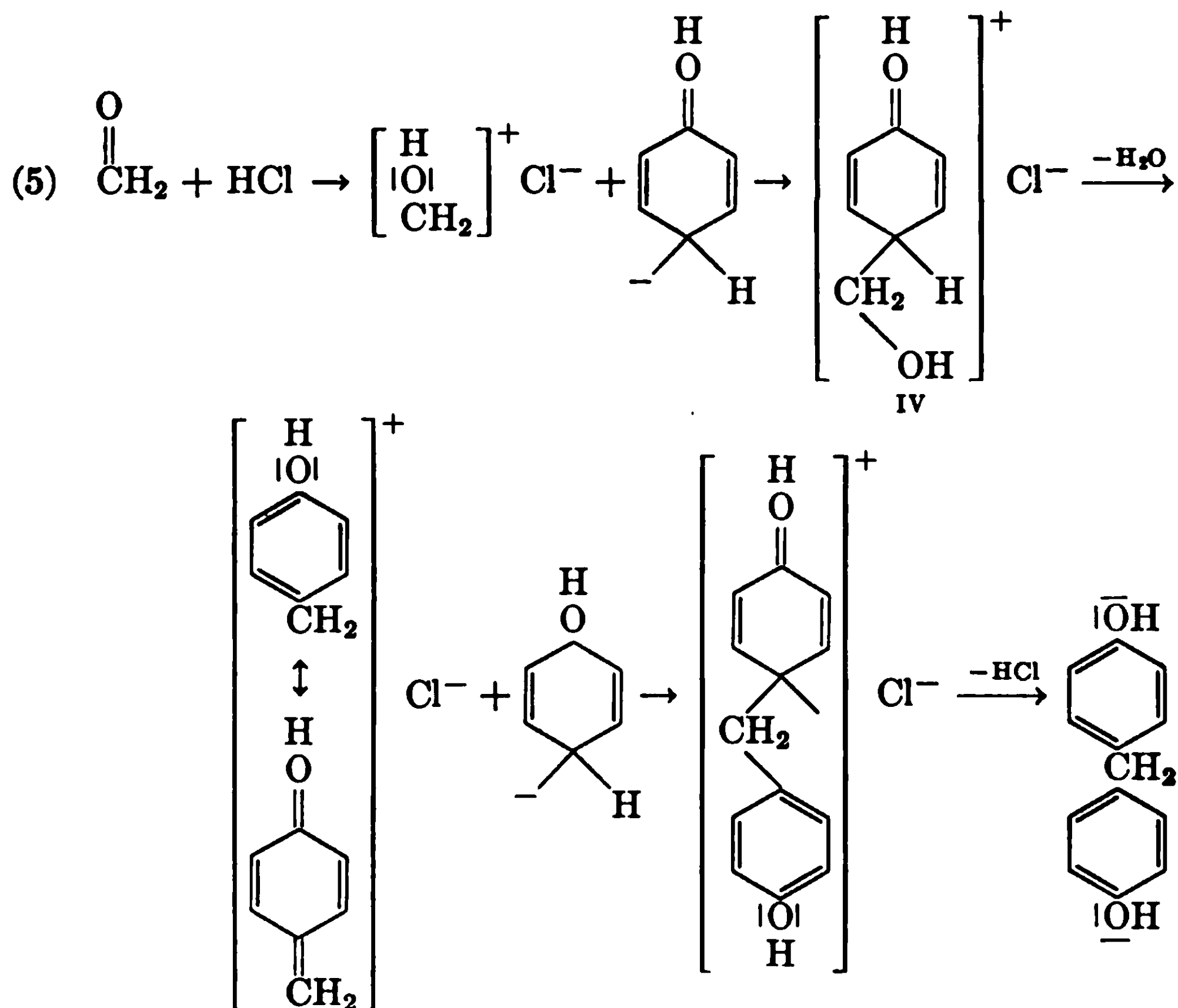
Assuming that phenol alcohols are intermediates in the formation of dihydroxydiphenylalkanes, the final step in the reaction in the presence of excess phenol would be the condensation of the phenol alcohol with more phenol accompanied by the elimination of a mole of water.

According to Pepper⁶⁷ the reaction occurs by the formation of a carbonium ion from the phenol alcohol, which then reacts with more phenol present in the system, reaction 4. Lilley⁶⁸ shows essentially the



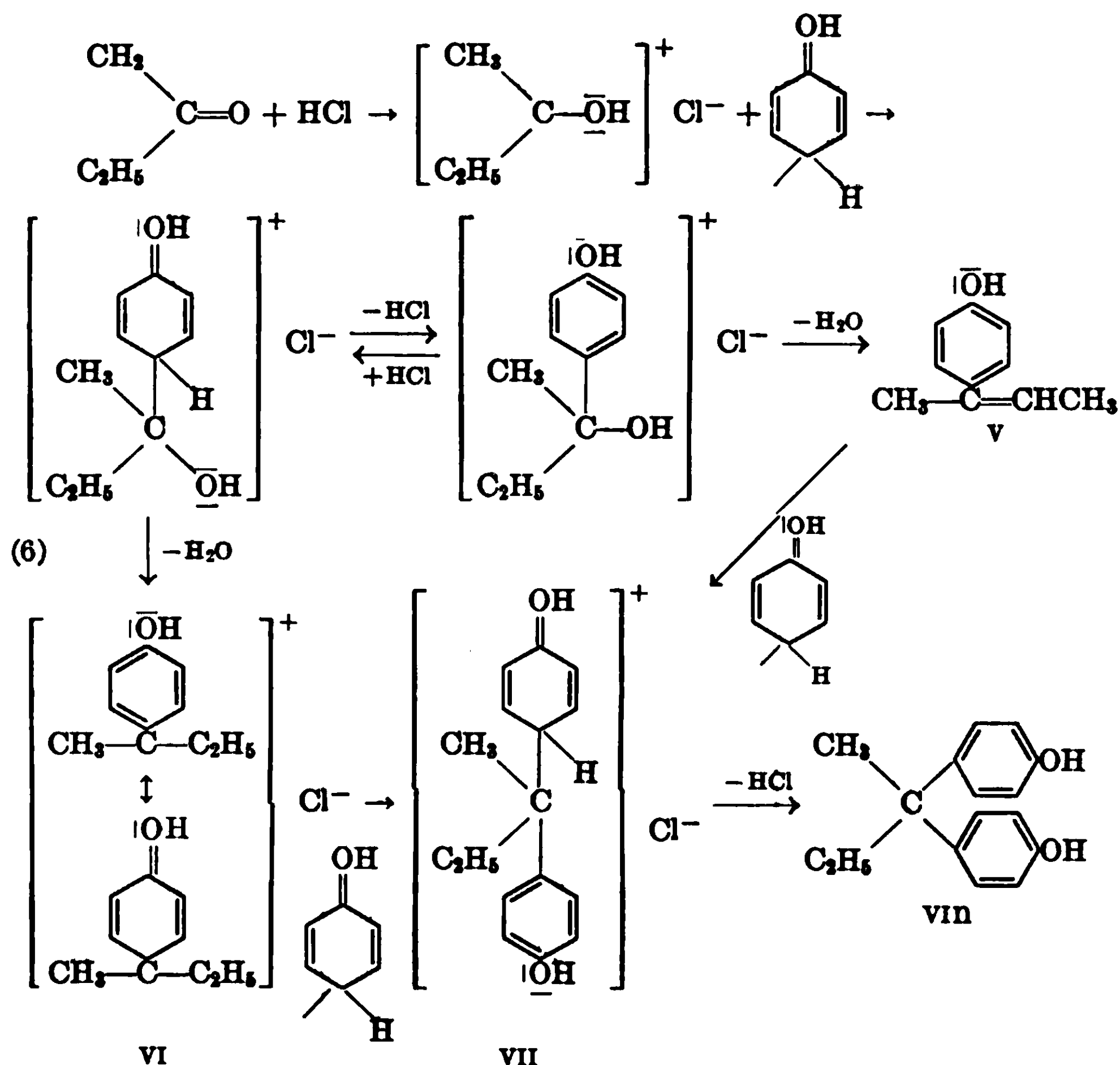
same mechanism except that the proton is shown adding first to the methylol group, which then loses water to form the hydroxybenzyl carbonium ion.

Opposed to the views expressed above are those of Hultsch, who thinks that the phenol alcohol, as such, need never be formed.^{69,70} According to Hultsch the dihydroxydiphenylalkane may result by reaction of an ionic intermediate derived from a quinone methide with the oxonium form of another phenol molecule, reaction 5. This



mechanism resembles those already discussed, except that the conversion of adduct IV to a free phenol alcohol is by-passed in the latter mechanism. Reaction conditions, such as concentration of acid, solvents, and temperature, would be expected to exert an effect on the course of the reaction.

Leibnitz and Naumann⁷¹ have made a study of the condensation of ketones with phenols under acidic condition. In addition to dihydroxydiphenylalkanes they obtained small yields of isoalkenylphenols, V, which in turn react readily with phenols to give dihydroxydiphenylalkanes, VIII. These data suggest an alternative route to the dihydroxydiphenylalkanes, reaction 6. However, the formation of the isoalkenylphenols is probably only a side reaction. In other respects the mechanism suggested by Leibnitz and Naumann is essentially the same as that suggested by Hultsch.



The rate of reaction of formaldehyde with phenols under acidic conditions is dependent on the concentration of hydrogen ions below a *pH* of about 3 to 4.^{72, 73} Kakiuchi⁷⁴ thinks that the rate-determining step

is the activation of the formaldehyde into a carbonium cation. The heat of formation of a methylene bridge has been given as 13.7 kcal./mole when formed from *p*-cresol dialcohol and phenol and as 23 kcal./mole when formed directly from phenol and formaldehyde.^{75,76}

With highly reactive phenols the most satisfactory procedure for preparing dihydroxydiphenylmethanes is to add formaldehyde slowly to an excess of the phenol containing an acid. If stoichiometric quantities of the phenol and formaldehyde are used, resin predominates with the more reactive phenols. Koebner^{77,78} and also Vanscheidt⁸⁸ found that nearly 10 moles of phenol per mole of formaldehyde were required if the dihydroxydiphenylmethanes were to be obtained essentially free of resin. Dilution with a solvent also retards resin formation but is much less effective on a volume basis than dilution with phenol. The higher alkyl phenols, particularly those with *ortho* or *para* substituents, require smaller excesses of the phenol to depress resin formation, and phenols with negative substituents show little tendency towards resinification. With the latter phenols reaction in concentrated acids with stoichiometric quantities of phenol and aldehyde is frequently employed.

Dihydroxydiphenylalkanes from Formaldehyde

In considering the individual dihydroxydiphenylmethanes those from phenol are of greatest interest. Noelling and Herzberg⁷⁸ were the first to report the 4,4'-isomer. They separated the compound from the resinous products obtained by the reaction of 2 moles of phenol with 1 mole of formaldehyde in very dilute hydrochloric acid. These authors reported a melting point of 148°C., some 14 degrees below that of the pure compound, but there appears to be little doubt that they had the compound in question. The low melting point is not too surprising since small quantities of one isomer cause a marked drop in the melting point of another isomer.^{80,81} In 1923 Trautenberg⁸² isolated an isomeric product which Megson and Drummond⁸⁸ later identified as 2,4'-dihydroxydiphenylmethane. Morgan⁸⁴ also obtained 2,4'- and 4,4'-dihydroxydiphenylmethane at about the same time by the direct reaction of phenol and formaldehyde.

In studying the effect of catalysts on the phenol-formaldehyde reaction Seebach⁸⁸ separated some crystals from the resins obtained which indicated that hydrochloric acid favored the formation of 4,4'-dihydroxydiphenylmethane. When ammonia or magnesium oxide was used as a catalyst more of the 2,4'-isomer was found. Bender⁸⁷ reports that hydrochloric acid will give 2,2'-, 2,4'-, and 4,4'-dihydroxy-

diphenylmethane but that under some conditions the 4,4'-isomer is favored. Stager and Biert⁸⁶ claim that ammonium chloride gave mainly the 4,4'-isomer but that the addition of ammonia to the reaction mixture tended to favor the formation of 2,4'-dihydroxydiphenylmethane.

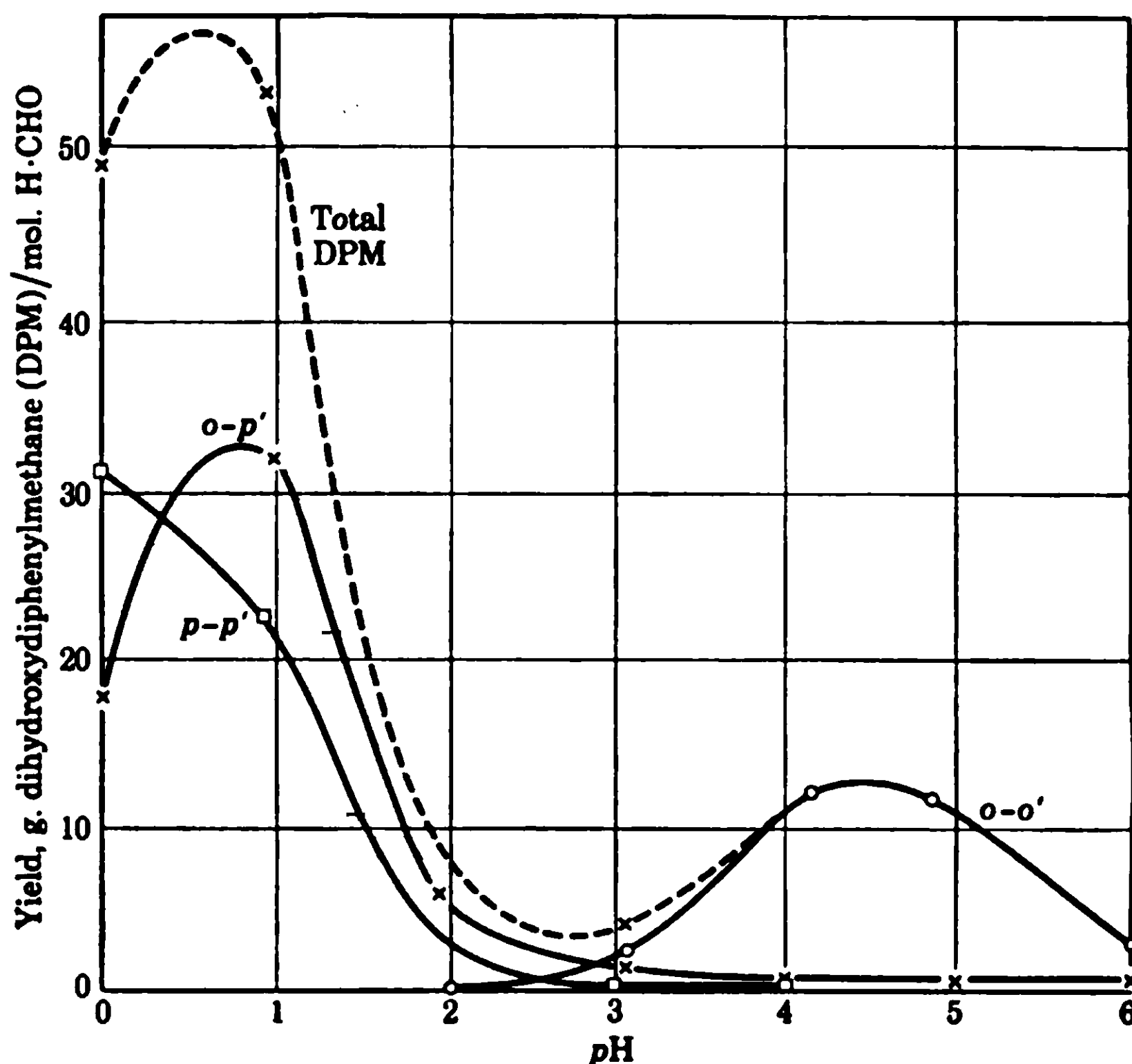


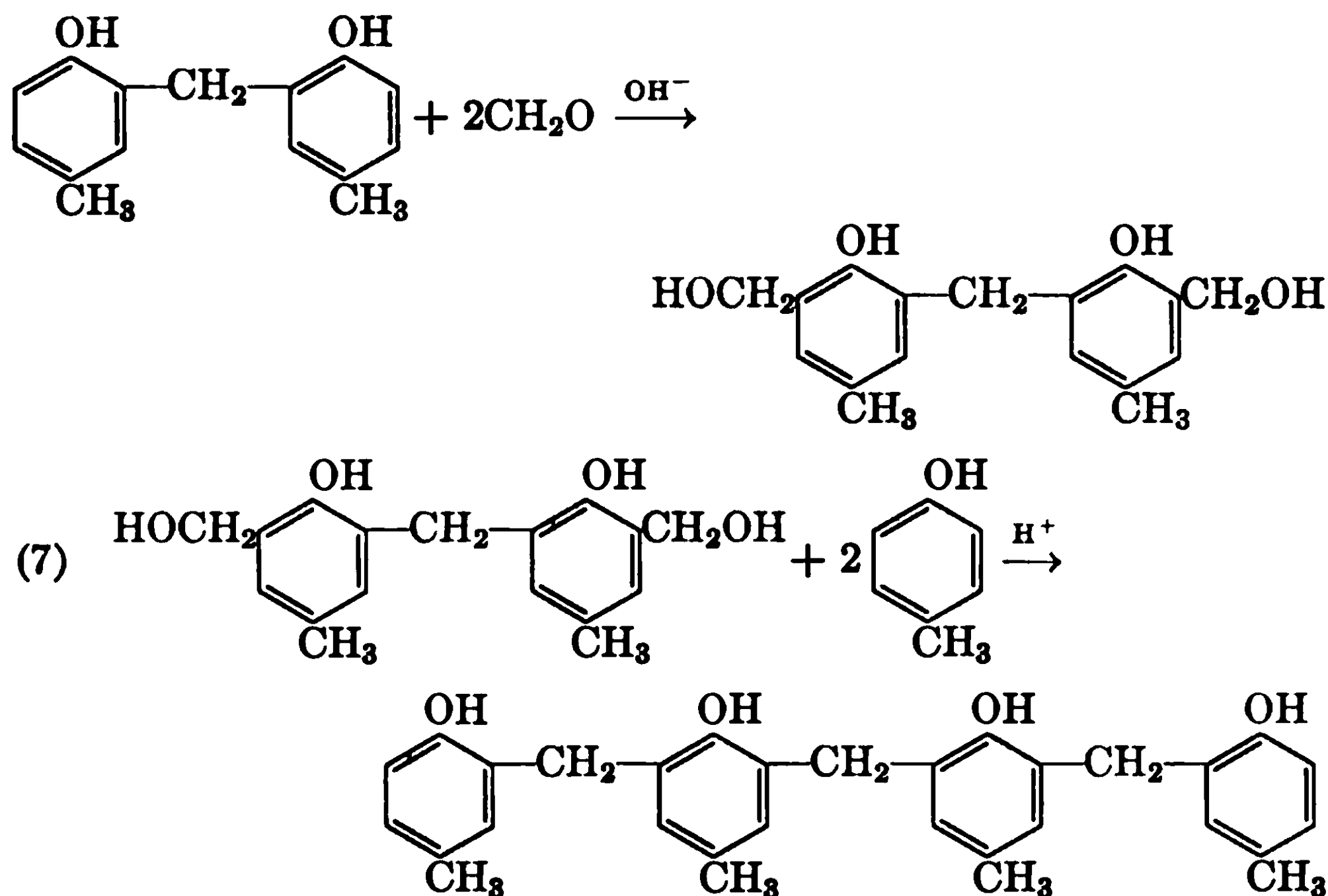
Fig. 1. Reprinted by permission of the authors, S. R. Finn and J. W. G. Musty, and by permission of the Controller of Her Britannic Majesty's Stationery Office. The illustration has a British Crown copyright.

At one time it was not considered possible to prepare 2,2'-dihydroxydiphenylmethane directly from phenol by reaction with formaldehyde, presumably because of the tendency of the compound to dehydrate to xanthene. That this assumption is incorrect has been demonstrated by Bender and his coworkers.^{81, 87, 88} The compound was obtained by reaction of an excess of phenol with formaldehyde at a high temperature in the presence of zinc, magnesium, or aluminum oxides as catalysts at a recommended pH between 4 and 7. Finn and Musty⁸⁹ have used buffered solution to study the effect of pH on the yield of isomeric dihydroxydiphenylmethanes. The yield of each isomer remaining after separation of some resin has been plotted in Fig. 1 as a function of pH. Inspection of the curves shows that the *p,p'*-isomer is the major crystalline product under strongly acidic conditions. At a slightly higher

*p*H the 2,4'-isomer is formed; the *p*H most favorable to formation of the 2,2'-isomer is between 4 and 5. Bender and also Finn and Musty found that reaction temperature has some effect on the quantity of each isomer formed. (See page 109 for a discussion of Bender's work.)

The cresols yield dihydroxyditolylmethanes under acidic conditions. *o*-Cresol gives mainly the 4,4'-dihydroxy-3,3'-dimethyldiphenylmethane, which may be separated as a crystalline compound after removal of the excess *o*-cresol.^{88, 90} *m*-Cresol under similar conditions forms a crystalline compound melting at 161°C., but the location of the methylene bridge has not been established.⁸⁸ The *p,p'*-isomer would normally be expected under strongly acidic conditions, but the methylene bridge might enter the 6-position because of blocking of the *para* position by the methyl group at the 3-position.

p-Cresol forms only one dinuclear compound. This makes its isolation a relatively simple matter. Koebner also has prepared the polynuclear compounds with two to seven nuclei, the hexa and hepta nuclear phenols being obtained only in crude form.^{77, 81} The synthesis of the tetranuclear derivative is illustrated in reaction 7. The com-

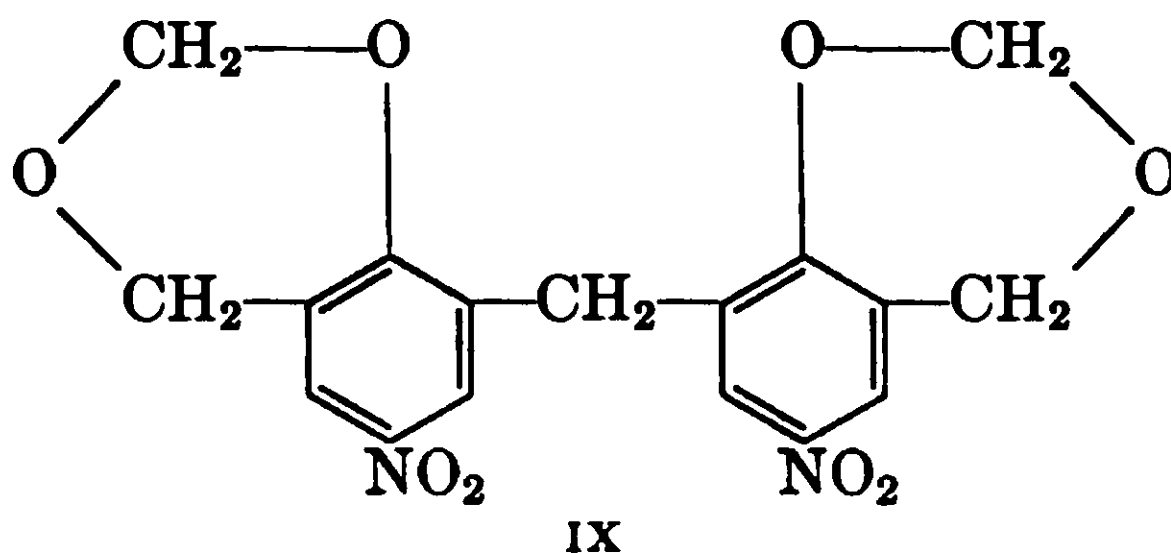


pounds having two to five nuclei were obtained in sufficient purity to give sharp melting points: dinuclear, 126; trinuclear, 215; tetranuclear, 173; and pentanuclear, 212–6°C.

The xylenols yield dinuclear methylene derivatives in much the same manner as the cresols. Morgan⁹² succeeded in preparing several isomeric methylene derivatives of both 3,4- and 3,5-xyleneol. Finn^{93, 94}

and Megson⁸⁸ have prepared several of the methylene derivatives of the xylenols. Under mild conditions 2,4- and 2,6-xyleneol give methylene derivatives, but under strongly acidic conditions resins may result. Mesityl gives a methylene derivative in spite of the fact that all the *ortho* and *para* positions are blocked. Megson^{94, 88} has shown that reaction occurs at the *meta* position.

Phenols containing negative substituents require high concentrations of catalysts for reaction. *Ortho*-, *meta*-, and *para*-nitrophenol give dihydroxydiphenylmethanes when reacted with formaldehyde using concentrated sulfuric acid as catalyst. Chattaway and Goepp⁹⁶ obtained 2,2'-dihydroxy-5,5'-dinitrodiphenylmethane by reaction of equimolar quantities of *p*-nitrophenol with formalin in concentrated sulfuric acid. With a little over 1.5 moles of formaldehyde per mole of nitrophenol the benzodioxan IX was obtained in almost quantitative yield.



Caro⁹⁷ prepared a methylene derivative of salicylic acid as early as 1892. Clemmensen and Heitman⁹⁸ apparently obtained the same compound by refluxing 2 moles of salicylic acid with 1 mole of formaldehyde in 50% sulfuric acid. Their product melted at 238°C.; Madsen⁹⁹ reports a melting point of 243–244°C. Methylene disalicylic acid has been offered in experimental quantities as a dibasic acid for use in alkyd resins.

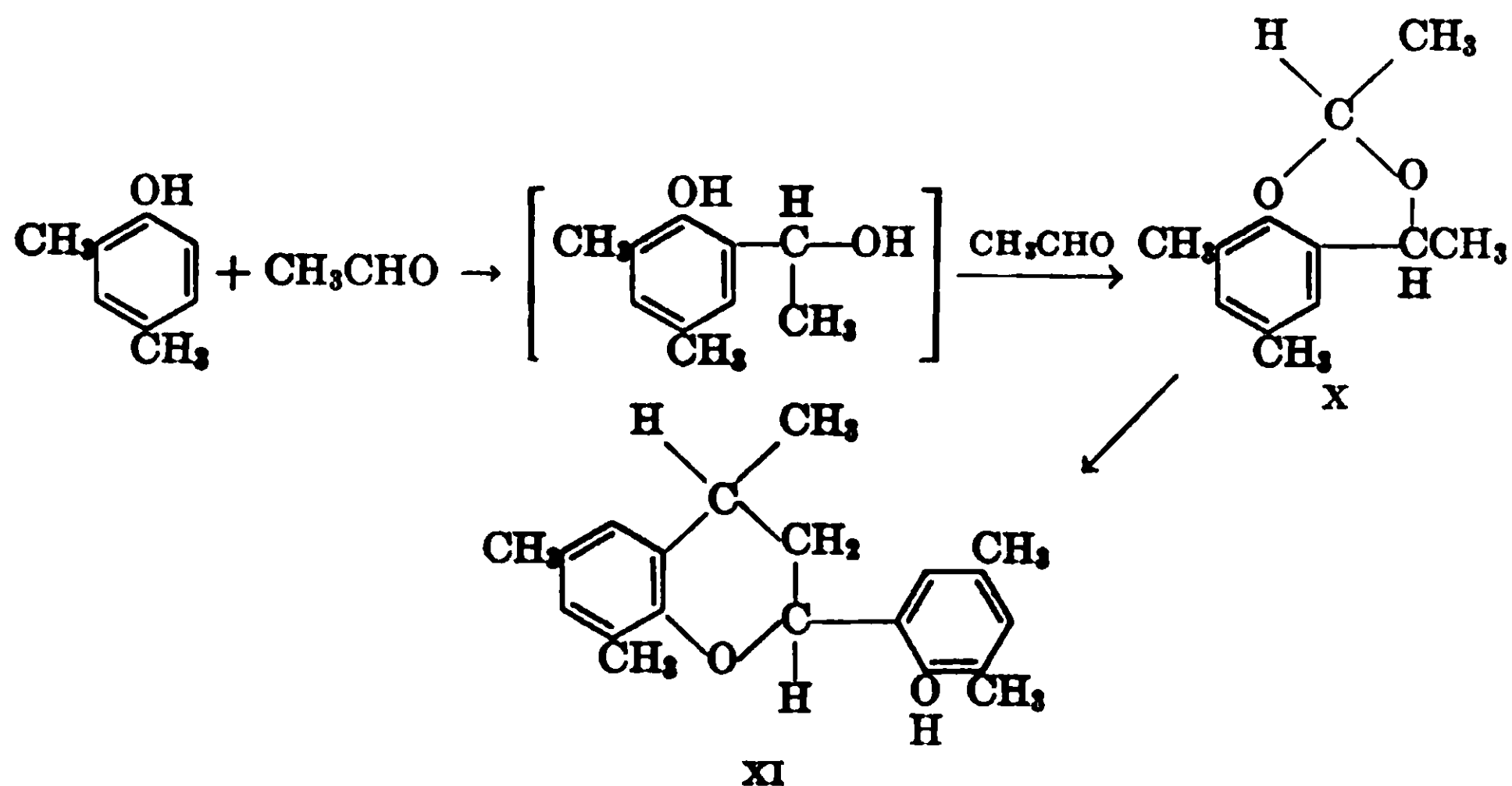
Polyhydric phenols, particularly those where the hydroxyl groups are *meta* to one another, are extremely reactive and require extensive dilution with an excess of the phenol or a solvent and reaction at a low temperature in order to minimize resinification. Caro⁹⁷ obtained a methylene derivative of resorcinol by reaction in very dilute hydrochloric acid. Möhlau and Koch¹⁰⁰ also obtained the same compound by reaction of 10 grams of resorcinol in 100 grams of 35% sulfuric acid with 3.5 grams of formaldehyde in the cold. The same authors also prepared methylene bisorcinol. According to Boehm,¹⁰¹ phloroglucinol does not condense with formaldehyde in the absence of a catalyst. With hydrochloric or sulfuric acid as catalyst a small yield of the methylene derivative and much resin were obtained. Methylene

bispyrogallol has been prepared by Caro ⁹⁷ using 20 parts of 10% hydrochloric acid to 1 part of formalin and 3 parts of pyrogallol.

Dihydroxydiphenylalkanes from Higher Aldehydes

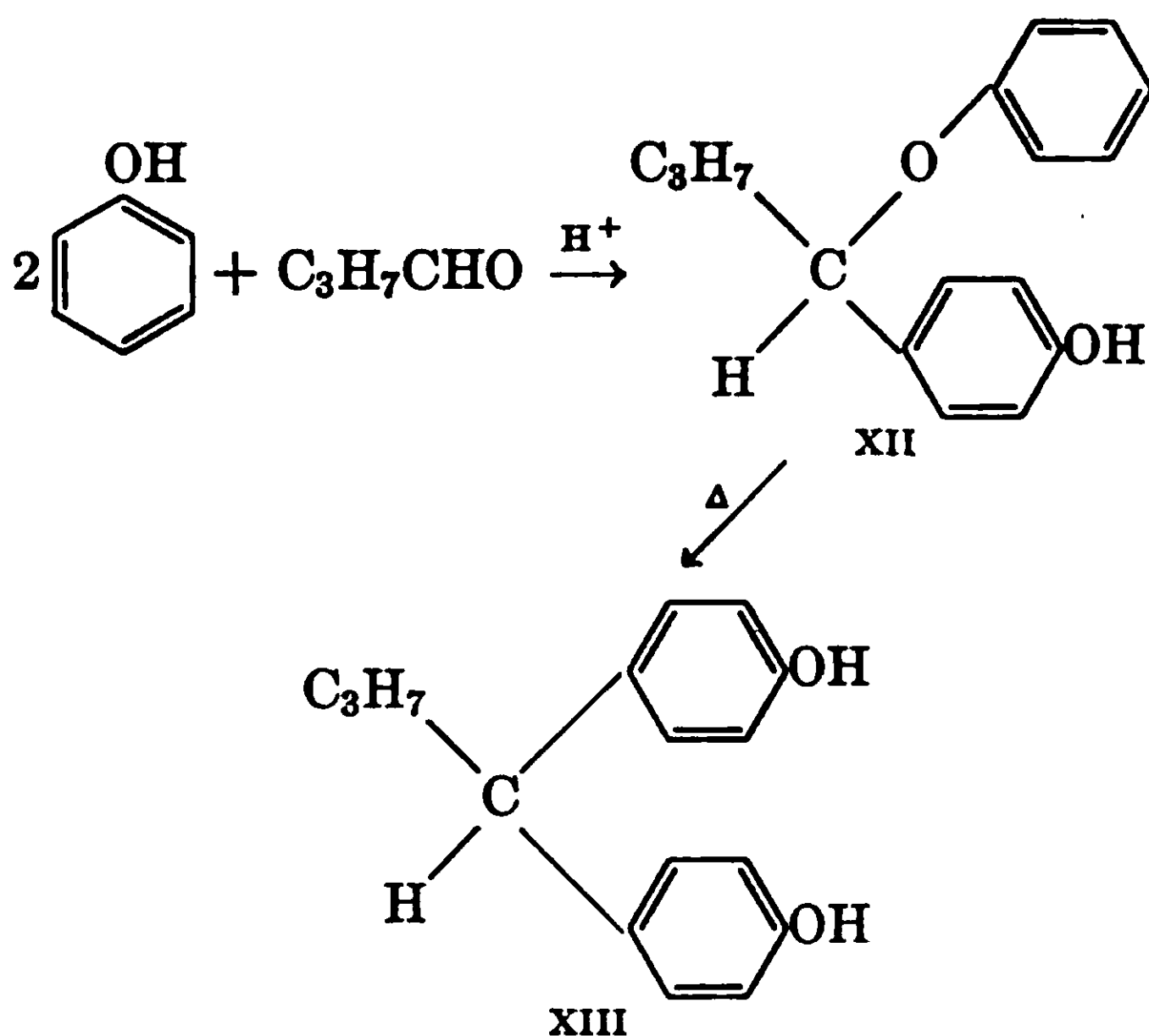
The higher aldehydes react with phenols in the presence of acids and catalysts of the Friedel-Crafts type to form dihydroxydiphenylalkanes. In order to avoid side reactions which will consume the aldehyde, reaction must be conducted under carefully controlled conditions since both the reaction temperature and the catalyst and catalyst concentration have profound effects.

With the exception of formaldehyde, acetaldehyde is one of the most reactive aldehydes. Baeyer ⁴³ included it in his early studies on the phenol-aldehyde reaction. Fabinyi ¹⁰² also reacted acetaldehyde in the form of the trimeric paraldehyde with phenol using stannic chloride as catalyst. By fractional distillation of the reaction mixture a crystalline dihydroxydiphenylethane was recovered. Claus and Trainer, ¹⁰³ Baekeland and Bender, ¹⁰⁴ Lunjak, ¹⁰⁵ and Niederl and McCoy ¹⁰⁶ have also studied the reaction of acetaldehyde with phenols but obtained largely resinous products. Upon adding concentrated hydrochloric acid to a cold solution of *p*-cresol and acetaldehyde in ethanol, Adler, Euler, and Gie ¹⁰⁷ obtained a dihydroxyditolythane. When 2,4'-dimethylphenol was substituted for *p*-cresol and the reactants, dissolved in benzene, were allowed to stand over 8 *N* hydrochloric acid a benzodioxan, X, was formed. Treatment of the benzodioxan with either strong alkali or acid presumably gave an *ortho* vinylphenol which dimerized to a chroman, XI. When X was heated over Frankonite at 400–650°C. the monomeric vinylphenols were obtained.



Propionaldehyde has not received the attention of some of the other lower aldehydes, but it reacts normally under acidic conditions to give dihydroxydiphenylpropanes.^{10, 15, 108}

Baekeland and Bender¹⁰⁴ studied the condensation of *n*-butyraldehyde with phenol using hydrochloric acid as catalyst. These authors thought that the primary reaction was the formation of 1-phenoxy-1-*p*-hydroxyphenylbutane, XII. Since dihydroxydiphenylbutane, XIII, was obtained in fairly good yield they concluded that the ether rearranged on heating. Briggs and Haworth⁸ condensed 2,4- and 2,5-dimethylphenol with butyraldehyde and used the compounds as antioxidants for rubber.



All the saturated aldehydes having up to seven carbon atoms have been reacted with a variety of phenols. They all give crystalline dihydroxydiphenylalkanes. The compounds are of interest for their germicidal, fungicidal, and antioxidant properties.^{10, 15, 108}

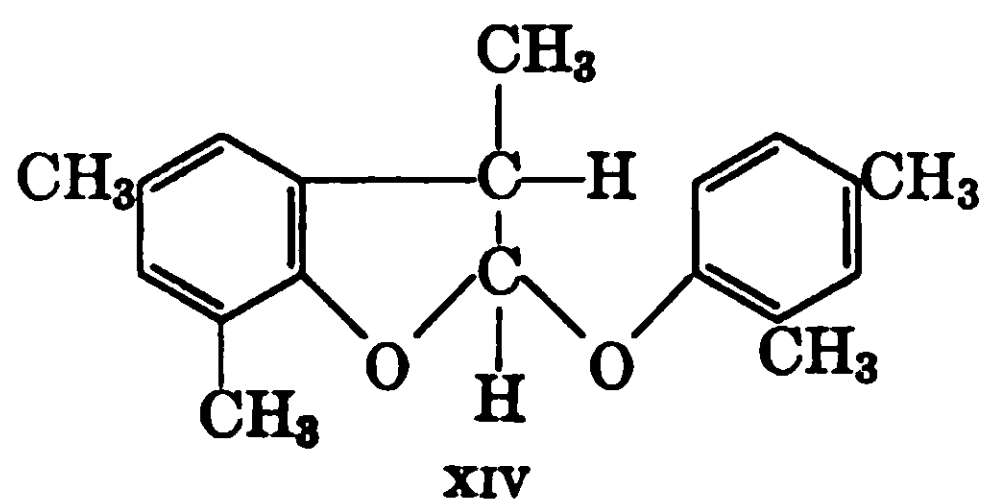
Chloral, furfural, and benzaldehyde are the most important aldehydes available commercially having no α hydrogen atoms. Chloral and benzaldehyde may be reacted with phenols in the presence of concentrated acids without serious side reactions, but furfural readily forms polymers with itself and must be handled under very mild conditions if resinification is to be avoided. As discussed in Chapter 2, under mildly acidic conditions a furylcarbinol⁶⁰ may be obtained, but the corresponding dihydroxydiphenylalkane from phenol and furfural has not been reported. However, the dihydroxydiphenylalkane from

2-*tert*-butyl-4-methylphenol, bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl) furylmethane, has been described.⁸

The condensation of chloral with various phenols has been studied rather extensively.¹⁰⁹⁻¹¹³ Chattaway and coworkers¹¹⁴⁻¹¹⁷ have several publications dealing with condensations in sulfuric acid, but under the conditions used benzodioxans were usually obtained. However, Harden and Reid¹⁸ condensed phenol and *o*-, *m*-, and *p*-cresol and thymol with chloral and invariably obtained crystalline dihydroxydiphenylalkanes.

Benzaldehyde forms dihydroxytriphenylmethanes on reaction with phenols. Phenol,⁴⁴ pyrogallol,⁴⁴ phloroglucinol,¹¹⁸ and 2,6- and 2,4-dimethylphenol¹⁰⁶ have been used in such condensations. Losev and Akutin⁸¹ studied the condensation of phenol and benzaldehyde at a 2 to 1 ratio and found that dihydroxytriphenylmethane and benzaurin were obtained. A series of triphenylmethanes also has been obtained by the condensation of phenols with hydroxybenzaldehydes.^{118a}

Of the unsaturated aldehydes, acrolein has received the greatest attention, having been used for the preparation of some of the early phenolic resins.¹¹⁸⁻¹²¹ The acrolein often was generated in the reaction mixture from glycerol. Adler and Tingstam¹²² were among the first to study the reaction of acrolein with phenols under carefully controlled conditions. With 2 moles of 2,4-dimethylphenol to 1 mole of acrolein in acetic acid solution, with hydrochloric acid as catalyst, compound XIV was formed as the major product.



The condensation of crotonaldehyde with 2,6-dimethylphenol has been studied by Niederl and McCoy.¹⁰⁸

Dihydroxydiphenylalkanes from Ketones

The preparation of dihydroxydiphenylalkanes from phenols and ketones requires careful control of reaction conditions if side reactions are to be held to a minimum. Liebnitz and Naumann,⁷¹ who reviewed much of the early patent literature, have given details as to the best procedures for the reaction of the lower dialkyl ketones with phenols.

In general, temperatures ranging from 25° to 60°C. were recommended. Hydrogen chloride has been used most frequently as catalyst.

According to the patent literature, mercaptans, mercapto acids, and hydrogen sulfide have a beneficial effect on the yield and purity of the dihydroxydiphenylalkane.^{29, 123, 124} A thioacetal or thiohemiacetal which is more reactive and less susceptible to side reactions than the free ketone presumably forms as an intermediate in the presence of the sulfur compounds. Dihydroxydiphenylalkanes may, in fact, be obtained by reaction of mercaptals or mercaptols with phenols.¹²⁵ Boron compounds also are claimed to have a beneficial effect on the purity of dihydroxydiphenylalkanes prepared in contact with these materials.¹²⁶

In the reaction with phenols, ketones show a greater tendency than aldehydes to stop at the bisphenol stage without the use of a large excess of phenol. Reaction occurs mainly at the *para* position of the phenol if one is available. If the *para* position is blocked, reaction will occur at an *ortho* position. When acetone is reacted with phenol under the proper conditions, the major product will be 4,4'-dihydroxydiphenyldimethylmethane. Commercial grades of this bisphenol may contain 3–5% of the 2,4'-isomer along with 2–4% of a trinuclear product and a small amount of 2-methyl-2(4-hydroxyphenyl)-4,4-dimethylchroman, sometimes referred to as codimer.

The manufacture of bisphenols from the lower ketones is attractive commercially since the amount of resin formed may be kept low and the major product is often largely a single isomer. The compound derived from acetone and phenol, known commercially as bisphenol-A, is a large-volume chemical with several suppliers. This bisphenol is finding use not only in conventional phenolic resins but also in the manufacture of polyepoxide resins. It was reported by Dianin in 1891.¹²⁷

According to Coggeshall¹²⁸ and Ambelang and Binder¹⁰⁸ dihydroxydiphenylalkanes may exist in different rotational configurations. The particular configuration assumed by the dihydroxydiphenylalkanes will depend on the degree of hydrogen bonding between the phenolic hydroxyl groups and also on steric factors. Although *cis* and *trans* isomers are ordinarily thought of as stable isomers involving compounds with carbon-carbon double bonds, the authors listed above have used the terms to designate different spatial arrangements of the phenol rings about a methylene or substituted methylene bridge. If the two phenolic hydroxyl groups of a 2,2'-dihydroxydiphenylalkane are oriented so that there is intramolecular hydrogen bonding between them the compound is referred to as being in the *cis* form. In

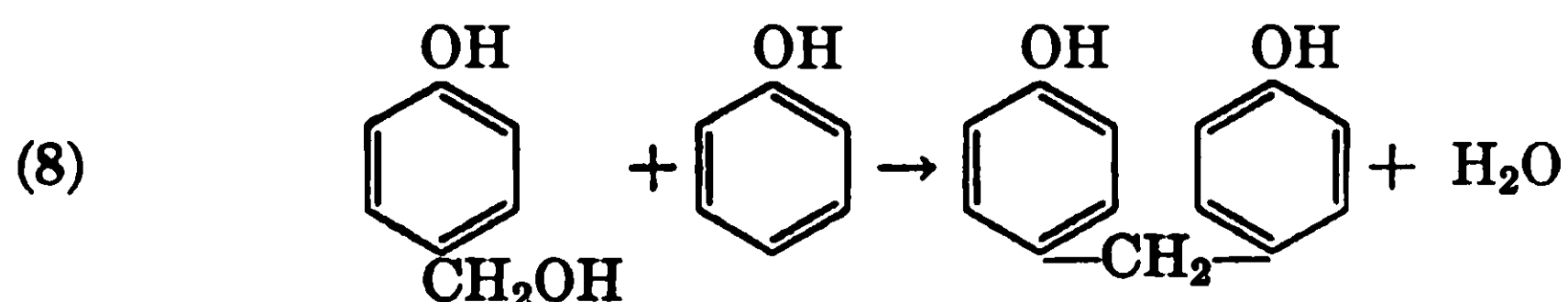
the *trans* form there is no intramolecular interaction between the phenolic hydroxyl groups although intermolecular interaction is not ruled out.

Sprengling^{123a} found that the first hydroxyl group of a 2,2'-dihydroxydiphenylmethane was hyperacid but that the second hydroxyl group shows little acidity. The hydroxyl groups of other dinuclear phenols show no such hyperacidity. These results also were explained on the basis of hydrogen bonding between the 2,2'-phenolic hydroxyl groups.

BASE-CATALYZED CONDENSATIONS

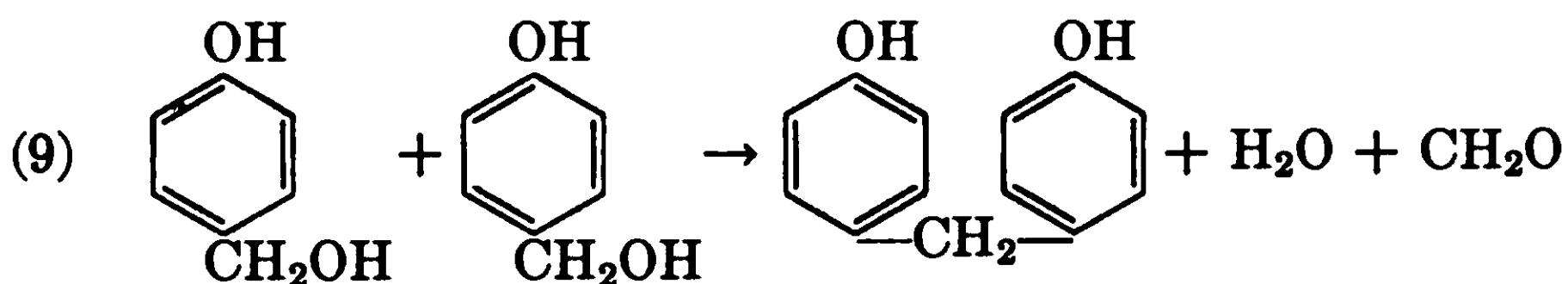
Dihydroxydiphenylalkanes can be obtained by the direct reaction of phenols with certain aldehydes under basic conditions. Although the products may be identical with those formed with acidic catalysts, the mechanism of reaction is apparently much different. Phenol alcohols are the first products formed in the reaction when basic catalysts are employed. If the phenol alcohol is relatively stable under alkaline conditions the reaction may tend to stop at this stage. Saligenin, for example, may be boiled with 5% aqueous caustic and be recovered with little or no loss on neutralizing the solution. However, most phenol alcohols do not exhibit such stability and may be converted to dihydroxydiphenylalkanes by continued heating with aqueous caustic.¹²⁹⁻¹³⁴ In general, phenol alcohols with *para* methylol groups show a greater tendency towards conversion to a methylene derivative than those with an *ortho* methylol group. As might be expected, phenols which are capable of reacting readily with formaldehyde to form a methylol derivative are usually equally capable of forming a methylene derivative. 2,6-Dimethylphenol, 2,4,5-trimethylphenol, 2,4,6-trimethylolphenol, and β -naphthol are particularly susceptible to rapid conversion to a methylene derivative under alkaline conditions.^{132, 135}

Dihydroxydiphenylalkanes presumably could be formed by either of two mechanisms under alkaline conditions. The formation of an intermediate phenol alcohol is assumed in either mechanism. The phenol alcohol could react with free phenol in the system to give a methylene derivative as shown in reaction 8, or reaction could occur



between the methylol groups of two phenol alcohols and be accom-

panied by the elimination of a mole of formaldehyde and a mole of water, reaction 9. Mechanism 9, although long considered unim-



portant, now appears the more likely of the two under alkaline conditions.^{39, 51, 70, 133, 135}

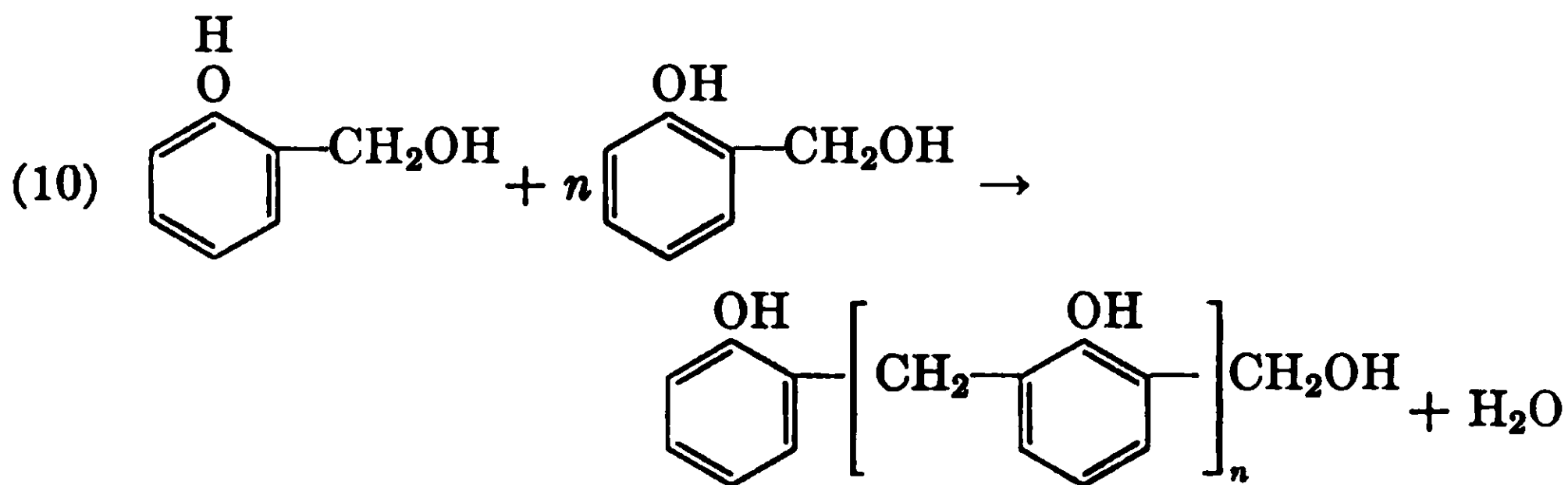
In general, basic catalysts are useful in preparing dihydroxydiphenylalkanes only with formaldehyde or aldehydes having no α hydrogens. Reaction under basic conditions has an advantage over reaction in the presence of acids with phenols, such as eugenol, which have unsaturated alkyl substituents that might be affected by acidic catalysts. Alkaline conditions also are favored for the conversion of durenol to a methylene derivative since acids tend to split the methylene derivative.

SELF-CONDENSATION OF PHENOL ALCOHOLS

A variety of products, including dihydroxydiphenylalkanes, may be obtained by the self-condensation of phenol alcohols. The type of product obtained depends, among other things, on whether acidic, basic, or neutral conditions are employed. By the thermal condensation of phenol alcohols, dibenzyl ethers are formed as the primary product, but these products on further heating may break down to methylene derivatives. However, the yields are not high under such conditions on account of numerous side reactions which consume the dibenzyl ethers.

The self-condensation of phenol alcohols under alkaline conditions is more likely to give a dihydroxydiphenylmethane free of by-products than under other conditions, but even here the reaction conditions must be carefully selected. This reaction has been discussed in the previous section.

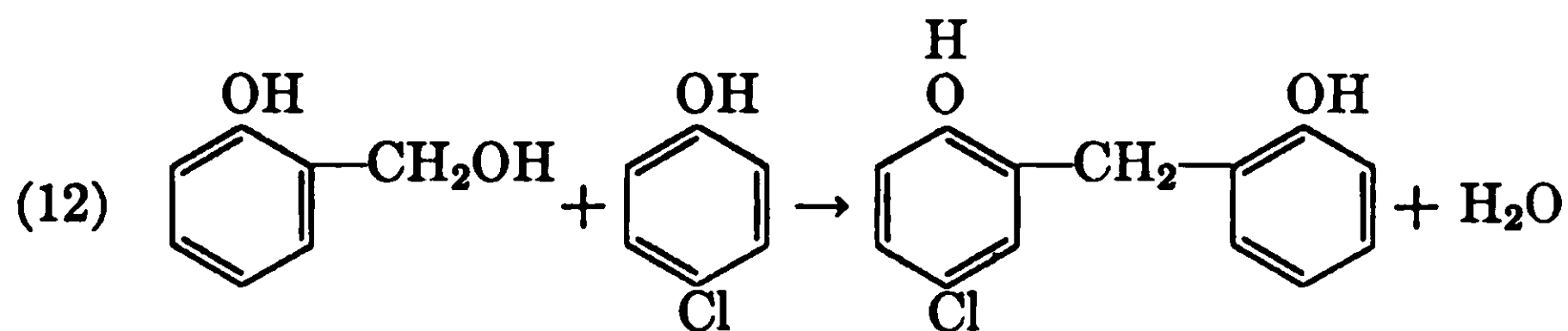
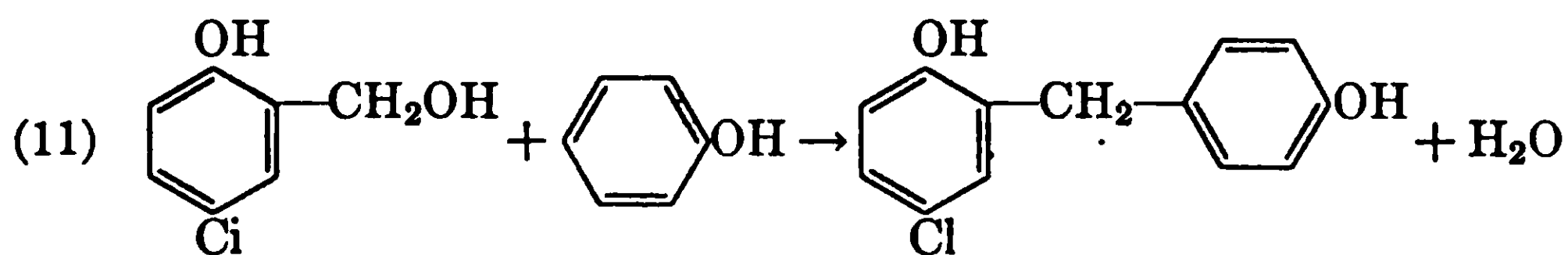
When acidic reagents are added to phenol alcohols, dihydroxydiphenylalkanes are obtained in appreciable yields only when the phenol alcohol is obtained from a monofunctional phenol.^{59b, 134} With phenol alcohols derived from polyfunctional phenols, a very serious side reaction is the formation of polynuclear products, reaction 10. The



escape of formaldehyde and the formation of methylene derivatives during the acid cure of casting resins, which are made with 2 to 2.5 moles of formaldehyde per mole of phenol, are well established. A similar reaction occurs under alkaline conditions in an aqueous solution.¹³⁶

CONDENSATION OF PHENOL ALCOHOLS WITH PHENOLS

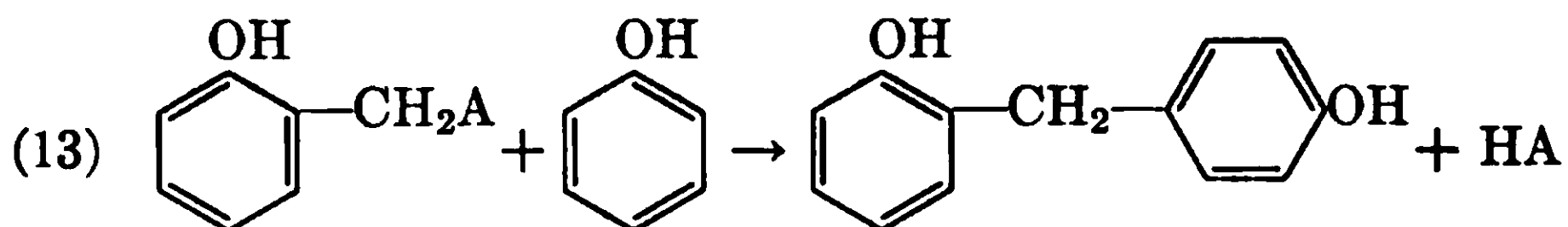
The preparation of dihydroxydiphenylalkanes by the condensation of phenol alcohols with phenols is surpassed in importance only by the direct condensation of phenols with aldehydes or ketones under acidic conditions. The former reaction has the advantage that unsymmetrical dihydroxydiphenylalkanes are readily prepared. Normally the phenol alcohol is prepared separately and then added slowly to an excess of the desired phenol in an acidic medium. Acetic acid is an excellent solvent for such reactions, and hydrogen chloride, either anhydrous or aqueous, is frequently used as catalyst.^{22, 52, 136-138} The preparation of 2,4'-dihydroxy-5-chlorodiphenylmethane and 2,2'-dihydroxy-5-chlorodiphenylmethane is shown below, reactions 11 and 12. These examples



were selected to show how it is possible, by the proper choice of reactants, to prepare in almost pure form not only an unsymmetrical dihydroxydiphenylmethane but a particular isomer as well. Since strongly

acidic conditions are normally used, the methylol group reacts with the phenol mainly at the *para* position if one is available. If the *para* position is blocked, reaction then occurs *ortho* to the phenolic hydroxyl group of the phenol. Where the phenol is polyreactive, resins or chain polyphenols are often formed along with varying amounts of the dihydroxydiphenylmethanes.

The condensation of other hydroxybenzyl compounds with phenols is analogous to the reaction of phenol alcohols with phenols. The general reaction is shown in equation 13; A represents a halogen, alkoxy, amino, or acyloxy group, etc.

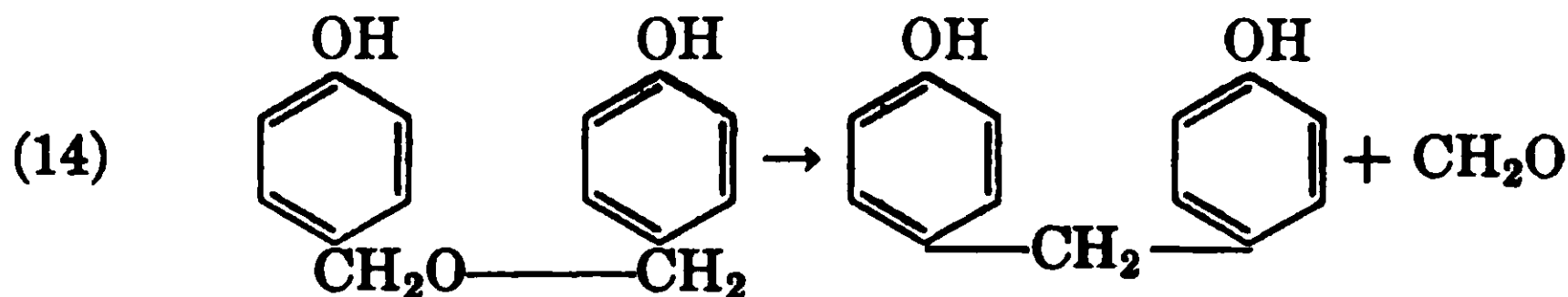


Ziegler^{32, 137} has investigated the reaction of halomethyl phenols with phenols in some detail. He thinks that, in the reaction of phenol alcohols with phenols where a halogen acid is employed as catalyst, a halomethyl phenol is first formed and it in turn reacts with the phenol. Sulfuric acid presumably may function in a similar manner by formation of an intermediate sulfate ester.

Where A is an alkoxy or acyloxy group the reactions generally require elevated temperatures and an acidic catalyst. On the other hand, where A is an amino or substituted amino group, a basic material has greater catalytic activity.¹³⁹ Besides the phenol alcohols only the halomethyl phenols have received much attention as starting materials for the synthesis of dihydroxydiphenylmethanes. The compounds where A represents other groups often are less reactive and may also be more expensive to prepare than the halomethyl phenols.

LOSS OF FORMALDEHYDE FROM DIHYDROXYDIBENZYL ETHERS

Phenol alcohols, derived from *ortho*- or *para*-substituted phenols, eliminate water and form dihydroxydibenzyl ethers when heated at 110–130°C. When the temperature is raised further, formaldehyde is lost and methylene derivatives, reaction 14, as well as other products are formed.



If a monofunctional phenol alcohol is used the yield of dihydroxydiphenylmethane may be fair. The reaction is catalyzed by both acids and bases.⁷⁰ Since the dibenzyl ethers are not easily prepared and the reaction is always accompanied by side reactions, the reaction is only of theoretical interest for the preparation of dihydroxydiphenylmethanes.

REACTION OF QUINONE METHIDES WITH PHENOLS

Because of their high reactivity, quinone methides derived from the polyfunctional phenols have not been isolated as monomeric materials although they may be obtained as dimers and trimers. Hultzs⁷⁰ has been a strong proponent of quinone methides as intermediates in the formation of many phenol-aldehyde products, among which he has included the methylene derivatives. According to Hultzs, the acid-catalyzed condensation of phenols with aldehydes and ketones need not involve the phenol alcohol step. Instead a quinone methide is formed which immediately reacts with more phenol to give the methylene derivative. This mechanism has been discussed (pages 9–10). Where the dimeric and trimeric quinone methide has already been formed, there is some evidence that these compounds may react with phenols to give dihydroxydiphenylmethanes, but the yields are very small.⁷⁰

REARRANGEMENT OF AROMATIC ACETALS OR HEMIACETALS


The rearrangement of aromatic acetals strictly speaking does not belong in a discussion of phenol-aldehyde reactions since acetals can seldom be prepared directly from phenols and aldehydes. Mixed acetals such as methylphenyl formal have been separated in small quantities from among the products of the acid catalyzed action of phenol and formaldehyde in methanol.^{140,141} Aromatic acetals are normally prepared by reaction of metallic phenates with methylene dihalides in a sealed tube. However, hemiacetals from aldehydes such as chloral are known.⁵⁰ On treatment with acids the acetals and hemiacetals undergo a vigorous reaction in which dihydroxydiphenylalkanes, resin, and aurin or similar products are obtained.^{142,143}

REACTION OF ACETYLENE WITH PHENOLS

Adler¹⁴⁴ has reviewed the early work on the reactions of phenols with acetylenes and has studied in detail the reactions of 2,4-dimethylphenol with acetylene. Depending on reaction conditions the dihy-


.... CH ₃	OH	OH	CH ₃	121	85
								126	149
								126-127.5	150
CH ₃	OH	CH ₃	CH	161	82
								162	86
								163-164	150
CH	CH ₃	OH	CH ₃	163	93
								164.5-166	152
OH	CH ₃ CH ₃	OH	OH ₂ CH ₃	167	93
OH	CH ₃ CH ₃	OH	CH ₃	152	152
OH CH ₃	CH ₃	OH	CH ₃	144	7
								148	130
								146	185
								145-146	150
CH ₃	CH	CH ₃	CH ₃	CH	CH ₃	150
....	CH ₃	CH	CH ₃	CH	CH ₃	175	158
								175	157
....	CH ₃	CH	CH ₃	OH	181-182	158
CH	CH ₃	CH ₃	CH	CH ₃	CH ₃ CH ₃	146	150
CH ₃ CH	CH ₃	CH ₃	CH ₃ CH	CH ₃	158	150
CH ₃ CH ₃	CH	CH ₃	CH ₃ CH ₃ CH ₃	CH	CH ₃	CH	CH ₃	214-215	161
CH ₃	CH	i-C ₃ H ₇	OH ₂	CH	i-C ₃ H ₇	162-164	14
								160-161	162
CH ₃	OH	C ₃ H ₇	CH ₃	OH	C ₃ H ₇	15
OH	CH ₃	i-C ₄ H ₉	OH	CH ₃	131-132	4
OH	i-C ₄ H ₉	CH ₃	OH	i-C ₄ H ₉	125-128	7

Table I. Dihydroxydiphenylmethanes (Continued)

Parent Compound	Position of Substituents										M. P., °C.	Refer- ences	
	2	3	4	5	6	2'	3'	4'	5'	6'			
	OH	OH ₂	<i>t</i> -C ₄ H ₉	OH	OH ₂	<i>t</i> -O ₄ H ₉	126-127	7	
	OH ₂	OH	<i>t</i> -C ₄ H ₉	OH ₂	OH	<i>t</i> -C ₄ H ₉	178.7-179.2 174-175	10 108	
	OH ₂	OH	<i>t</i> -O ₄ H ₉	OH ₂	OH	<i>t</i> -C ₄ H ₉	169.5-108	108	
	OH	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	OH	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	142-143 145.5-146	7 53	
	OH	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	OH ₂	OH	OH	<i>t</i> -O ₄ H ₉	<i>t</i> -C ₄ H ₉	CH ₃	215.3-216.3 208-209	10 108
	OH	OH ₂	Cyclo-C ₆ H ₁₁	OH	OH ₂	Cyclo-C ₆ H ₁₁	106-108	169	
	OH	Cyclo-C ₆ H ₁₁	OH ₂	OH	Cyclo-C ₆ H ₁₁	CH ₃	153.5-155.5	53	
	OH	OCH ₃	OCH ₃	OH	119-120	181	
	OCH ₃	OH	OCH ₃	OH	107-108 107-108	180 181	
	OH	OCH ₃	—CH ₂ CH=CH ₂	OH	OCH ₃	—CH ₂ CH=CH ₂	84	130	
	OH	Cl	OH	128-129	164	
	OH	Cl	OH	Cl	177-178	153	
	Cl	OH	Cl	OH	103-104 103	169 167	

OH	Cl	Cl	OH	Cl	Cl	166-167	18
										166-167	26
										168	50
										168	166
....	Cl	OH	Cl	Cl	OH	Cl	184-185	166
										185-186	169
OH	Cl	Cl	Cl	OH	Cl	Cl	Cl	164-165	18
										161-162	26
OH	OH ₂	Cl	OH	CH ₃	Cl	195.2-196.4	10
....	CH ₃	OH	Cl	OH ₂	OH	Cl	157-157.3	10
OH	Cl	Cl	OH	OH ₂	CH ₃	166	137
OH	CH ₃	Cl	OH	CH ₃	Cl	180-182	14
OH	CH ₂ Cl	CH ₃	OH	OH ₂ Cl	CH ₃	135	137
OH	<i>i</i> -C ₃ H ₇	Cl	OH	Cl	Cl	123-126.8	22
OH	<i>sec</i> -C ₄ H ₉	Cl	OH	Cl	Cl	110.5-111	22
OH	Cl	<i>t</i> -C ₄ H ₉	OH	Cl	<i>t</i> -C ₄ H ₉	123.2-126.7	10
OH	<i>i</i> -C ₃ H ₇	Cl	CH ₃	OH	<i>i</i> -C ₃ H ₇	Cl	CH ₃	128-129	14
OH	<i>t</i> -C ₄ H ₉	Cl	CH ₃	OH	<i>t</i> -C ₄ H ₇	Cl	OH ₂	181.6-182.5	10
OH	<i>i</i> -C ₃ H ₇	Cl	OH	<i>t</i> -C ₄ H ₉	CH ₃	158-159	14
OH	<i>i</i> -C ₃ H ₇	Cl	CH ₃	CH ₃	CH ₃	OH	<i>i</i> -C ₃ H ₇	174-176	14
OH	<i>i</i> -C ₃ H ₇	Cl	CH ₃	OH	Cl	134.5-135.5	14
OH	C ₆ H ₁₁	Cl	OH	Cl	Cl	Cl	182.6	192
OH	C ₆ H ₁₁	Cl	OH	Cl	Cl	176-178.5	192
OH	<i>p</i> -ClC ₆ H ₄ CH ₂ -	Cl	OH	Cl	Cl	Cl	156-167	192
OH	C ₆ H ₅ CH ₃	Cl	OH	Cl	Cl	146-147.5	192

Table I. Dihydroxydiphenylmethanes (Continued)


Parent Compound	Position of Substituents										M.P., Refer-	
	2	3	4	5	6	2'	3'	4'	5'	6'	°C.	ences
	OH	Cl	Br	Cl	OH	Br	Br	Cl	166-166.5	18
OH <i>i</i> -C ₃ H ₇	Cl	Cl	OH	Cl	Br	125.5-128	82
OH <i>i</i> -C ₃ H ₇	Cl	Cl	OH	Br	Br	124.5-125	82
OH <i>i</i> -C ₃ H ₇	Cl	Cl	OH	I	<i>t</i> -C ₄ H ₉	CH ₃	126-127	14
OH I	Cl	Cl	OH	I	Cl	195-196	14
OH SO ₃ H	Cl	Cl	OH	Cl	14
OH SO ₃ H	Cl	Cl	OH	SO ₃ H	Cl	14
OH NO ₂	Cl	Cl	OH	NO ₂	Cl	181-182	14
OH NH ₂	Cl	Cl	OH	NH ₂	Cl	230-232	14
OH NHCOCH ₃	Cl	Cl	OH	NHCOCH ₃	Cl	228-229	14
OH	Br	Br	OH	155	170
OH	Br	Br	OH	Br	182-183	18
....	CH ₃	OH	Br	CH ₃	OH	Br	183-184	184
OH Br	CH ₃	CH ₃	OH	Br	CH ₃	202	83

DIHYDROXYDIPHENYLALKANES

CH ₃ Br	OH CH ₃	CH ₃ Br	OH CH ₃	152-153 151-153	153 173
OH Br	CH ₃ CH ₃	OH Br	CH ₃	165	100
OH Br	CH ₃ CH ₃	OH Br	CH ₃ CH ₃	143	160
OH Br Br	OH	172-174	17
OH Br Br	OH	OH	198-199 202	17 172
OH Br Br OH	OH	157-159	172
.... Br	OH Br	OH OH	200	174
.... Br	OH Br	OH	OH	182-183	174
.... Br	OH Br OH	OH	147-148	174
OH Br Br CH ₃	OH	154-155	17
OH Br Br	OH	CH ₃	135-137	17
OH Br Br	OH I I	199-200	17
OH Br Br	OH CH ₃ Br	190-199	17
.... Br	OH Br Br	OH Br	226-227	183
OH Br Br Br	OH Br	199	83
OH Br Br	OH Br Br	195-197 198-199	17 18
CH ₃ Br	OH Br	CH ₃	CH ₃ Br	OH Br	CH ₃	246	171
OH Br Br	OH Br Br	CH ₃	157-158	17
OH Br Br	Br	OH Br Br	Br	180	18
OH CH ₂ Br	CH ₃ CH ₃	OH OH ₂ Br CH ₃	CH ₃	170 d.	160

Table I. Dihydroxydiphenylmethanes (Continued)

Parent Compound	Position of Substituents										M.P., °C.	Refer- ences
	2	3	4	5	6	2'	3'	4'	5'	6'		



.... CH ₃	OH	CH ₂ Br	CH ₃	OH	OH ₂ Br	138	175
OH	OH	OH	203.5-204.6	176	
OH	OH	OH	CH ₃	CH ₃	226-227	177	
OH	OH	OH	OH	150-151	14	
									250	15	
OH	OH	OH	OH	OH	OH	OH	241 d.	97	
OH	OH	OH	OH	OH	OH	240	16	
.... COOH	OH	OH	COOH	OH	239	15	
									243-244	99	
OH NO ₂	OH	NO ₂	268	98	
.... CH ₃	OH	NO ₂	OH ₂	OH	NO ₂	217	160	
									217	178	
OH —AsO ₃ H	OH	—AsO ₃ H	>300	14	
OH C ₆ H ₅ N ₂ —	OH	174	179	
OH	NO ₂ C ₆ H ₄ N ₂ — OH ₂	OH	OH	CH ₃	201-202	179	
OH	NO ₂ C ₆ H ₄ N ₂ — CH ₃	OH	NO ₂ C ₆ H ₄ N ₂ —	CH ₃	268	179	
OH	C ₆ H ₅ N ₂ —	CH ₃ CH ₃	CH ₃ CH ₃	OH	C ₆ H ₅ N ₂ —	CH ₃ CH ₃	205	179	
OH	NO ₂ C ₆ H ₄ N ₂ —	CH ₃ OH ₂	OH	OH	NO ₂ C ₆ H ₄ N ₂ —	CH ₃ CH ₃	197	179	
OH	C ₆ H ₅ N ₂ — CH ₃	CH ₃	CH ₃	OH	C ₆ H ₅ N ₂ —	218	179	

Table II. Dihydroxydiphenylalkanes


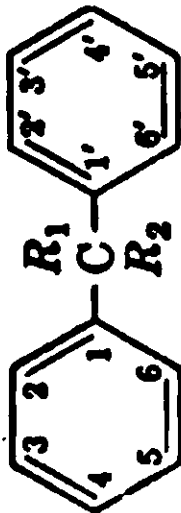
Parent Compound	Position of Substituents												M.P., °C.	Refer- ences
	R ₁	R ₂	2	3	4	5	6	2'	3'	4'	5'	6'		
	H	CH ₃	OH	OH	122	15
													122	102
	H	CH ₃	CH ₃	OH	CH ₃	OH	188	15
	H	CH ₃	OH	CH ₃	OH	CH ₃	141	107
	H	CH ₃	CH ₃	OH	OH ₂	CH ₃	OH	CH ₃	143	100
	H	CH ₃	OH	CH ₃	CH ₃	OH	CH ₃	133	106
													135-135.5	144
	H	CH ₃	CH ₃	OH	<i>t</i> -C ₂ H ₇	CH ₃	OH	<i>t</i> -C ₂ H ₇	188	162
	H	CH ₃	CH ₃	OH	<i>t</i> -C ₄ H ₉	CH ₃	OH	<i>t</i> -C ₄ H ₉	001.1-201.5	10
													195-196	108
	H	CH ₃	OH	Cl	OH	Cl	170-171	14
	H	CH ₃	OH	I	Cl	OH	I	123-124.5	14
	H	CH ₃	Br	OH	NO ₂	Br	OH	NO ₂	172	62
	H	CH ₃	Br	OH	Br	Br	OH	Br	140-141	62
	H	CH ₃	Br	NO ₂	OH	Br	Br	NO ₂	OH	Br	145	62
	H	CH ₃	Br	Br	OH	Br	Br	Br	OH	Br	169-170	62
	H	OH ₂	Br	Br	OH	Br	NO ₂	Br	Br	OH	Br	NO ₂	233	62

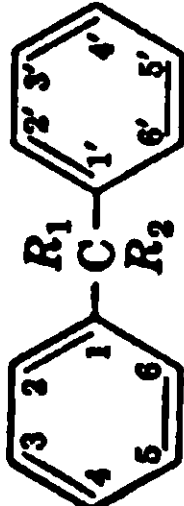
Table II. Dihydroxydiphenylalkanes (Continued)

Parent Compound		Position of Substituents										M.P., Refer- °C. ences	
R ₁	R ₂	2	3	4	5	6	2'	3'	4'	5'	6'		
H	CH ₃	Br	Br	OH	Br	Br	Br	Br	OH	Br	Br	227-228	68
H	C ₂ H ₅	OH	OH	129	15
H	C ₂ H ₅	OH	OH	OH	OH	>300	15
H	C ₂ H ₅	CH ₃	OH	CH ₃	OH	94	15
H	C ₂ H ₅	CH ₃	OH	CH ₃	OH	145	15
H	C ₂ H ₅	CH ₃	OH	l-C ₄ H ₉	OH ₂	OH	l-C ₄ H ₉	190-190.4	10
												189-190	108
H	C ₃ H ₇	OH	OH	137	15
H	C ₃ H ₇	CH ₃	OH	CH ₃	OH	145	15
H	C ₃ H ₇	OH ₂	OH	CH ₃	OH	135	15
H	C ₃ H ₇	OH	OH ₂	CH ₃	OH	CH ₃	CH ₃	129	8
												123	11
H	C ₃ H ₇	CH ₃	OH	CH ₃	CH ₃	OH	CH ₃	171-173	8
												171-173	11
H	C ₃ H ₇	OH	CH ₃	l-C ₄ H ₉	OH	CH ₃	l-C ₄ H ₉	130.8-131.5	10
H	C ₃ H ₇	OH	l-C ₄ H ₉	CH ₃	OH	l-C ₄ H ₉	CH ₃	126.4-127.2	10
H	C ₃ H ₇	CH ₃	OH	l-C ₄ H ₉	CH ₃	OH	l-C ₄ H ₉	210-210.7	10
												207.5-208	108



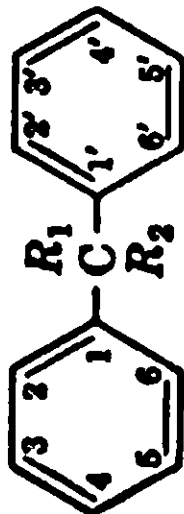
H	C ₂ H ₇	CH ₃	CH	n-C ₄ H ₉	CH ₃	OH	n-C ₄ H ₉	121.4-123	10
H	C ₂ H ₇	OH t-C ₄ H ₉	t-C ₄ H ₉	CH ₃ CH	t-C ₄ H ₉	t-C ₄ H ₉	OH ₂	123.5-124.1	10
H	C ₂ H ₇	CH ₃	OH	t-C ₄ H ₉	CH ₃	OH	t-C ₄ H ₉	162.8-168.6	10
H	C ₂ H ₇	OH	OH	OH	OH	>300	15
H	t-C ₃ H ₇	CH ₃	OH	t-C ₄ H ₉	CH ₃	OH	t-C ₄ H ₉	229.8-230.7	10
										228.5-229	168
H	t-C ₃ H ₇	OH t-C ₄ H ₉	CH ₃	OH t-C ₄ H ₉	OH ₂	188-189	5
H	t-C ₃ H ₇	OH t-C ₄ H ₉	t-C ₄ H ₉	CH ₃ OH	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	118.1-118.6	10
H	C ₄ H ₉	CH	OH	120	15
										186	104
H	C ₄ H ₉ CH ₃	OH	CH ₃	OH	97	15
H	C ₄ H ₉	CH ₃	OH	CH ₃	OH	149	15
H	C ₄ H ₉	CH	OH	OH	OH	>300	15
H	C ₂ H ₁₁	OH	OH	110.5	15
H	C ₂ H ₁₁ CH ₃	OH	CH ₃	OH	78	15
H	O ₂ H ₁₁	CH ₃	OH	OH ₂	OH	152	15
H	C ₂ H ₁₁	OH	OH	OH	OH	>300	15
H	(C ₂ H ₅) ₂ CH	CH ₃	OH	t-C ₄ H ₉	OH ₂	OH	t-C ₄ H ₉	196-196.5	108
H	O ₂ H ₁₃	CH	OH	120	15
H	C ₂ H ₁₃ CH ₃	OH	CH ₃	OH	68	15
H	O ₂ H ₁₃	CH ₃	OH	CH ₃	OH	186	15
H	C ₂ H ₁₃	CH ₃	OH	t-C ₄ H ₉	CH ₃	OH	t-C ₄ H ₉	188.5-159	108
H	C ₂ H ₁₃	CH	OH	OH	OH	>300	15

Table II. Dihydroxydiphenylalkanes (Continued)

Parent Compound	Position of Substituents											M.P., °C.	References
	R ₁	R ₂	2	6	5	6	2'	3'	4'	5'	6'		
	H	OH ₂ C(CH ₃)CH ₃ -CH ₂ -CH CH ₃	OH	CH ₃	CH ₃	OH	OH ₂	CH ₃	169-170	9
H	H	(CH ₃) ₂ CC(CH ₃) CH ₃ 	CH ₃	<i>t</i> -C ₄ H ₉	CH ₃	OH	<i>t</i> -C ₄ H ₉	166-167	108
H	H	C ₄ H ₉ (O ₂ H ₅)CH-	OH ₂	<i>t</i> -C ₄ H ₉	CH ₃	OH	<i>t</i> -C ₄ H ₉	109
H	Cy	-C ₆ H ₁₁ CH ₂ -	OH	146.5-147.3	27
H	CH ₂ Cl	CH ₃	CH ₃	<i>t</i> -C ₄ H ₉	OH ₂	OH	<i>t</i> -C ₄ H ₉	228.5-229.5	10
H	CCl ₃	OH	202	109
H	CCl ₃	OH	202	111
H	CCl ₃	CH ₃	CH ₃	OH	121-122	15
H	CCl ₃	CH ₃	CH ₃	OH	162-109	15
H	CCl ₃	OH ₂	CH ₃	CH ₃	OH	OH ₂	176-176	153
H	OCl ₃	CH ₃	<i>t</i> -C ₂ H ₇	OH ₂	OH	<i>t</i> -C ₂ H ₇	193.5	15
H	CCl ₃	CH ₃	<i>t</i> -C ₄ H ₉	CH ₃	OH	<i>t</i> -C ₄ H ₉	218.9-219.3	10
H	CCl ₃	OCH ₃	OCH ₃	OH	98	109
H	CCl ₃	OH	NO ₂	OH	NO ₂	179	113

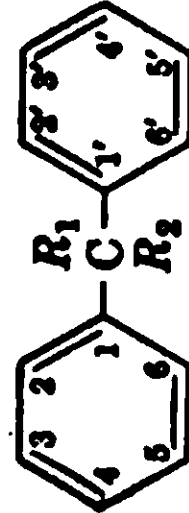
H	CCl ₃	OH Cl	Cl	OH Cl	Cl	185-186	186
H	CCl ₃	OH Cl	Cl	OH Cl	Cl	106
H	CH ₃ CHClCH ₂ - CH ₃	OH	CH ₃ OH ₂	OH	CH ₃	199	106
H	CH ₃ CHClCH ₂ -	OH OH ₂	CH ₃	OH CH ₃	CH ₃	152	106
H	HC-CH HC C-	CH ₃	OH	t-C ₄ H ₉	OH ₂	OH	t-C ₄ H ₉	223.3-223.7	10
H	HC-CH HC C-	OH t-C ₄ H ₉	CH ₃	OH t-C ₄ H ₉	OH ₂	3
H	C ₆ H ₅ CH ₃	OH	CH ₃ CH ₃	OH	CH ₃	131	106
H	C ₆ H ₅	OH CH ₃	CH ₃	OH CH ₃	OH ₂	163	106
H	C ₆ H ₅	CH ₃	OH	t-C ₄ H ₉	OH ₂	OH	t-C ₄ H ₉	199.3-106.8	10
H	C ₆ H ₅	OH t-C ₄ H ₉	CH ₃	OH t-C ₄ H ₉	OH ₂	171-172	1
H	C ₄ H ₉	OH	Cl	OH	Cl	168-169.5	14
H	C ₆ H ₅	OH I	Cl	OH I	Cl	193-194.5	14
H	C ₆ H ₅ Br	OH	Br	Br OH	Br	160-101	62
H	p-HOC ₆ H ₅	OH	OH	239-240	118a
H	p-HOC ₆ H ₅ CH ₃	OH CH ₃	OH	245-246	118a
H	p-HOC ₆ H ₅	CH ₃	OH	CH ₃	OH	205	118a
H	p-HOC ₆ H ₅	CH ₃	OH	t-C ₄ H ₉	CH ₃	OH	t-C ₄ H ₉	262.4-263	10

Table II. Dihydroxydiphenylalkanes (Continued)

Parent Compound	Position of Substituents												M.P., °C.	Refer- ences
	R ₁	R ₂	2	3	4	5	6	2'	3'	4'	5'	6'		
	H	$\text{CH}_3\text{C}(\text{CH}_3)\text{CH}_2$ $-\text{CH}_2-\text{CH}$ CH_3	CH	CH ₃	CH ₃	CH	CH ₃	CH ₃	169-170	9
	H	H $(\text{CH}_3)_2\text{CC}(\text{CH}_3)$ CH_3 	CH ₃	OH	<i>l</i> -C ₄ H ₉	CH ₃	OH	<i>l</i> -C ₄ H ₉	166-167	108
	H	$\text{C}_4\text{H}_9(\text{C}_2\text{H}_5)\text{CH}-$	CH ₃	OH	<i>l</i> -C ₄ H ₉	CH ₃	CH	<i>l</i> -C ₄ H ₉	108
	H	$\text{C}_7-\text{C}_8\text{H}_{11}\text{CH}_2-$	OH	OH	146.5-147.3	27
	H	CH_2Cl	CH ₃	OH	<i>l</i> -C ₄ H ₉	CH ₃	OH	<i>l</i> -C ₄ H ₉	228.5-229.5	10
	H	CCl_3	CH	OH	202	108
	H	CCl_3	CH ₃	CH	CH ₃	OH	202	111
	H	CCl_3	CH ₃	CH	CH ₃	OH	121-122	15
	H	CCl_3	CH ₃	OH	CH ₃	OH	162-108	15
	H	CCl_3	CH ₃	CH	CH ₃	CH ₃	OH	CH ₃	175-176	153
	H	CCl_3	CH ₃	OH	<i>l</i> -C ₄ H ₉	CH ₃	OH	<i>l</i> -C ₄ H ₉	193.5	15
	H	CCl_3	CH ₃	OH	<i>l</i> -C ₄ H ₉	CH ₃	OH	<i>l</i> -C ₄ H ₉	218.8-219.3	10
	H	CCl_3	OCH ₃	OH	OCH ₃	OH	08	108
	H	CCl_3	OH	NO ₂	OH	NO ₂	179	113

H	CCl ₃	OH	Cl	Cl	OH	Cl	Cl	185-106	163
H	CCl ₃	OH	Cl	Cl	Cl	CH	Cl	Cl	163
H	CH ₃ CHClCH ₂ -	OH ₂	OH	OH ₂	CH ₃	OH	CH ₃	199	106
H	CH ₃ CHClCH ₂ -	OH	CH ₃	CH ₃	OH	OH ₂	CH ₃	152	106
H	<div><div>HC-CH</div><div> </div><div>HO C-</div><div><div><div></div><div></div><div>S</div></div></div></div>	CH ₃	OH	<i>l</i> -C ₄ H ₉	CH ₃	OH	<i>l</i> -C ₄ H ₉	223.3-223.7	10
H	<div><div>HC-CH</div><div> </div><div>HC C-</div><div><div><div></div><div></div><div>O</div></div></div></div>	OH	<i>l</i> -C ₄ H ₉	CH ₃	OH	<i>l</i> -C ₄ H ₉	OH ₂	3
H	C ₆ H ₅	OH ₂	OH	CH ₃	CH ₃	OH	CH ₃	131	106
H	C ₆ H ₅	OH	CH ₃	OH ₂	OH	CH ₃	CH ₃	163	106
H	C ₆ H ₅	CH ₃	OH	<i>l</i> -C ₄ H ₉	CH ₃	OH	<i>l</i> -O ₄ H ₉	199.3-106.8	10
H	C ₆ H ₅	OH	<i>l</i> -C ₆ H ₉	CH ₃	CH	<i>l</i> -C ₆ H ₉	CH ₃	171-172	1
H	C ₆ H ₅	OH	Cl	OH	Cl	168-169.5	14
H	C ₆ H ₅	OH	I	Cl	OH	I	Cl	193-194.5	14
H	C ₆ H ₅	Br	OH	Br	Br	OH	Br	160-161	62
H	<i>p</i> -HOC ₆ H ₅	OH	CH	239-240	118a
H	<i>p</i> -HOC ₆ H ₅	CH ₃	OH	CH ₃	OH	245-246	118a
H	<i>p</i> -HOC ₆ H ₅	CH ₃	OH	CH ₃	OH	205	118a
H	<i>p</i> -HOC ₆ H ₅	CH ₃	OH	<i>l</i> -C ₄ H ₉	CH ₃	OH	<i>l</i> -C ₄ H ₉	262.4-263	10

Table II. Dihydroxydiphenylalkanes (Continued)

Parent Compound	Position of Substituents												M.P., Refer- ences
	R ₁	R ₂	2	3	4	5	6	2'	3'	4'	5'	6'	
	H	<i>m</i> -HOC ₆ H ₅	CH ₃	OH	CH ₃	OH	162 118a
	H	<i>o</i> -HOC ₆ H ₅	CH ₃	OH	OH ₂	OH	236 118a
	H	<i>o</i> -HOC ₆ H ₄	CH ₃	OH	<i>t</i> -C ₄ H ₉	CH ₃	OH	<i>t</i> -C ₄ H ₉	216.7-217 10
	H	<i>o</i> -CH ₃ OC ₆ H ₄	OH	OH	181-183 118a
	H	3,4-(CH ₃ O) ₂ C ₆ H ₃	CH ₃	OH	<i>t</i> -C ₄ H ₉	CH ₃	CH	<i>t</i> -C ₄ H ₉	231.2-231.9 10
	H	2-ClO ₂ H ₄	CH ₃	OH	<i>t</i> -C ₄ H ₉	CH ₃	OH	<i>t</i> -C ₄ H ₉	226.3-226.9 10
	H	2,4-Cl ₂ C ₆ H ₃	OH	CH ₃	CH ₃	OH	CH ₃	CH ₃	183.7-194.1 10
	H	2,5-Cl ₂ C ₆ H ₃	CH ₃	OH	<i>t</i> -C ₄ H ₉	CH ₃	OH	<i>t</i> -C ₄ H ₉	209.9-210.4 10
	H	2,5-(HO)ClC ₆ H ₃	CH ₃	OH	<i>t</i> -C ₄ H ₉	CH ₃	OH	<i>t</i> -C ₄ H ₉	214.2-215.9 10
	H	CH ₃ CO	CH ₃	OH	<i>t</i> -C ₄ H ₉	OH ₂	OH	<i>t</i> -C ₄ H ₉	196.2-197.1 10
	H	CH ₃ CH ₂ CH=C- CH ₃	CH ₃	OH	<i>t</i> -C ₄ H ₉	OH ₂	OH	<i>t</i> -C ₄ H ₉	190.1-190.5 10
	H	CH ₃ (CH ₂) ₂ CH=C- CH ₃	CH ₃	OH	<i>t</i> -C ₄ H ₉	CH ₃	OH	<i>t</i> -C ₄ H ₉	210.2-210.6 10
CH ₃	CH ₃		OH	OH	155 25 156.5 29

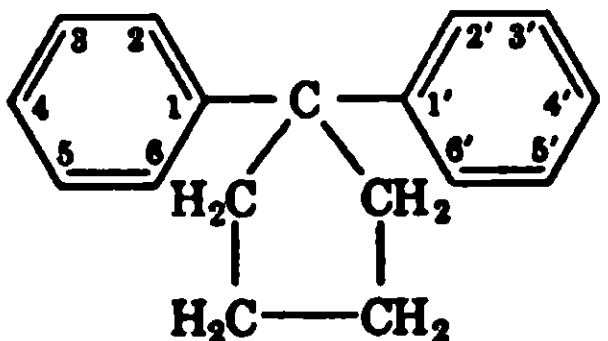
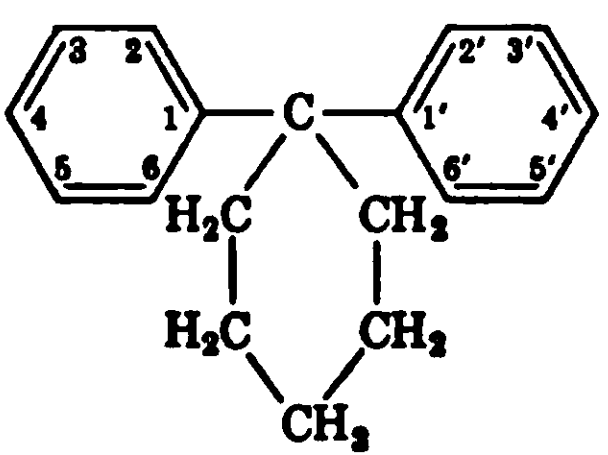
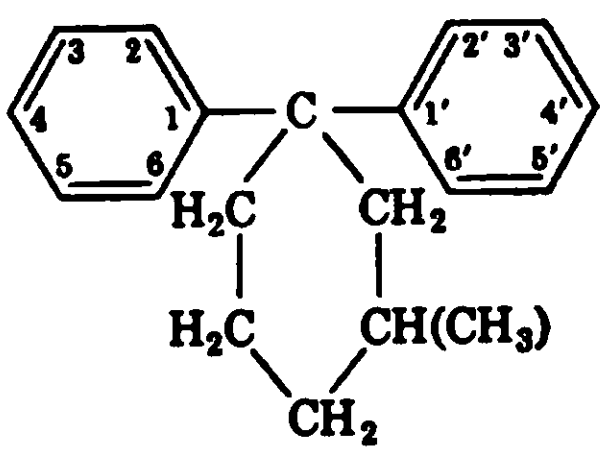
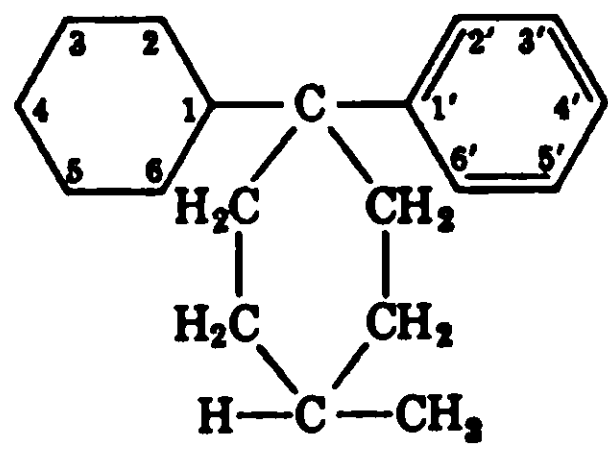

CH ₃	CH ₃	OH	OH
CH ₃	CH ₃	OH	CH ₃	OH	CH ₃	131-132 71
CH ₃	CH ₃ OH ₂	OH	OH	CH ₃	OH	135.5 29 136-137 71
CH ₃	CH ₃	OH	CH ₃ H ₇	OH	CH ₃ H ₇	96.5-97 1
CH ₃	CH ₃ CH ₃ H ₇	OH	OH	CH ₃ H ₇	OH	96.5-97 29
CH ₃	CH ₃ CH ₂ =CHOH ₂	OH	OH	CH ₂ =CH-OH ₂	OH	Liquid 29
OH ₂	CH ₃	OH CH ₃ H ₉	CH ₃	OH CH ₃ H ₉	CH ₃	161-162 6
CH ₃	CH ₃ CH ₃ H ₉	OH	OH	CH ₃ H ₉	OH	89-90 29
CH ₃	CH ₃	OH CH ₃ H ₉	CH ₃ H ₉	OH CH ₃ H ₉	CH ₃ H ₉	Liquid 7
CH ₃	CH ₃ CH ₃ H ₉	OH	OH	CH ₃ H ₉	OH	98-99 29
CH ₃	CH ₃ Br	OH	OH	Br	OH	NO ₂	176 184
CH ₃	CH ₃ Br	OH	OH	Br	OH	Br	162-163 184
OH ₂	OH ₂ NO ₂	OH	OH	NO ₂	OH	184 154
CH ₃	CH ₃ CH ₃	OH	OH	CH ₃	OH	NO ₂	195 184
CH ₃	CH ₃ NH ₂	OH	OH	NH ₂	OH	271 154
CH ₃	C ₂ H ₅	OH	OH	OH	125 71 125 185 126-127 185
CH ₃	C ₂ H ₅ CH ₃	OH	OH	CH ₃	OH	145-146 71 146 184
CH ₃	C ₂ H ₅	OH CH ₃ H ₉	CH ₃	OH CH ₃ H ₉	CH ₃	134.5-135.5 6
CH ₃	C ₂ H ₇	OH	OH	OH	149 25 149 185

Table II. Dihydroxydiphenylalkanes (Continued)

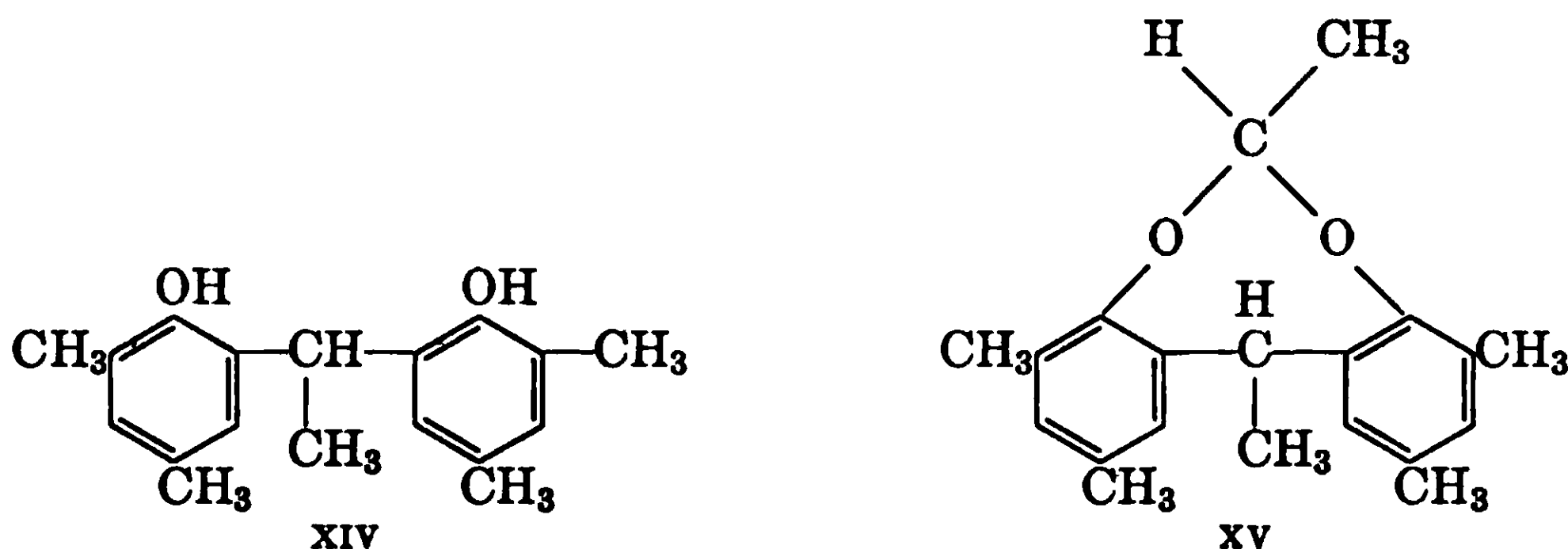
Parent Compound	Position of Substituents												M.P., Refer- ences	
	R ₁	R ₂	2	3	4	5	6	2'	3'	4'	5'	6'		
	CH ₃	i-C ₃ H ₇	OH	OH	194	25
	CH ₃	C ₄ H ₉	OH	OH	Liquid	25
	CH ₃	i-C ₄ H ₉	OH	OH	150	185
													154-155	186
	CH ₃	i-C ₄ H ₉	CH ₃	OH	CH ₃	OH	129	188
	CH ₃	C ₆ H ₁₁	OH	OH	101	85
	CH ₃	O ₆ H ₁₃	OH	OH	88	25
	CH ₃	C ₆ H ₅	OH	OH	188	85
													187-188	62
													175	185
	CH ₃	C ₆ H ₅	CH ₃	OH	CH ₃	OH	141	186
	CH ₃	CH ₃ C ₆ H ₄	OH	OH	151	185

CH ₃	p-CH ₃ OC ₆ H ₄	OH	OH	245	25
CH ₃	-CH ₂ CH ₂ COOH	OH	OH	173	191
CH ₃	CH ₃ CO	OH	OH	131-132 130	187 190
CH ₃	CH ₃ CO	CH ₃	OH	CH ₃	150-157	187
C ₂ H ₅	C ₂ H ₅	OH	OH	204 204-205	25 186
C ₂ H ₅	C ₂ H ₅ CO	OH	OH	201 Oil	71 189
C ₃ H ₇	C ₃ H ₇	CH	CH	154	25
C ₄ H ₉	C ₄ H ₉	CH	CH	170.5	25
C ₆ H ₁₁	C ₆ H ₁₁	OH	CH	148.5	25
C ₆ H ₅	C ₆ H ₅	OH	OH	202 285-290	62 104
C ₆ H ₅	C ₆ H ₅ CO-	CH	CH	212	190
C ₆ H ₅	C ₆ H ₅ C(OH)-	OH	CH	152-154	190
C ₆ H ₅ CH ₂ -	C ₆ H ₅ CH ₂ -	OH	OH	193	25

Table III. Dihydroxydiphenylcycloalkanes

Parent Compound	Position of Substituents										M.P., Refer- °C. ences	
	2	3	4	5	6	2'	3'	4'	5'	6'		
	OH	OH	157 156	25 185
	OH	OH	184 184	25 185
	CH3	OH	CH3	OH	186	185
	OH	OH	167	185
	OH	OH	178 180	25 185

droxydixylylethane XIV or the cyclic acetal XV was obtained. Both compounds can also be obtained by substituting acetaldehyde for acetylene.



Koresin, a rubber tackifier developed in Europe, is obtained by the reaction of acetylene with *t*-butylphenol. Chemical evidence and infrared absorption data indicate that the material is a polynuclear product in which the phenolic nuclei are joined by ethylidene bridges as in XIV.¹⁴⁸⁻¹⁴⁷

REDUCTION OF SELECTED KETONES

The reduction of dihydroxydiphenyl ketones under the proper conditions leads to the formation of dihydroxydiphenylmethanes. The reaction has very limited use since compounds with substituents on the methylene bridge of the dihydroxydiphenylmethane cannot be obtained and the necessary ketones are often difficult to prepare. Bender^{81,87} used the reaction to prepare 2,2'-dihydroxydiphenylmethane. The ketone was reduced catalytically with hydrogen over copper chromite or by the use of zinc amalgam.

REACTION OF DIHALOGEN COMPOUNDS WITH PHENOLS

The formation of dihydroxydiphenylalkanes from phenols and dihalogen compounds is a special case involving the alkylation of a phenol with an alkyl halide. Reactions of this type have been covered adequately elsewhere.

Pertinent references and the reported melting points for many of the known dihydroxydiphenylalkanes will be found in Tables I, II, and III.

REFERENCES FOR CHAPTER 3

- ¹ A. J. Dietzler, U. S. pat. 2,482,748 (1950).
- ² H. Morowitz, *Ind. Eng. Chem.*, 41, 1442-1447 (1949).

- ³ D. R. Stevens and A. C. Dubbs, U. S. pat. 2,515,908 (1950).
⁴ American Cyanamid Co., *New Product Bulletin* 16, 30 Rockefeller Plaza, New York, New York.
⁵ D. R. Stevens and A. C. Dubbs, U. S. pat. 2,515,907 (1950).
⁶ D. R. Stevens and A. C. Dubbs, U. S. pat. 2,515,906 (1950).
⁷ A. R. Davis and F. A. V. Sullivan, U. S. pat. 2,538,355 (1951).
⁸ A. S. Briggs and J. Haworth, U. S. pat. 2,559,932 (1951).
⁹ J. Haworth and A. Lambert, Brit. pats. 651,368 and 651,369 (1951).
¹⁰ D. J. Beaver and P. J. Stoffel, *J. Am. Chem. Soc.*, 74, 3410 (1952).
¹¹ A. S. Briggs and J. Haworth, Brit. pat. 621,004 (1949).
¹² D. W. Young, D. L. Cottle, and W. F. Fischer, U. S. pat. 2,625,568 (1953).
¹³ A. H. Craige, Jr., and A. L. Klecker, *N. Am. Veterinarian*, 27, 26 (1946).
U. S. pat. 2,480,556 (1949).
¹⁴ H. E. Faith, *J. Am. Chem. Soc.*, 72, 837 (1950); U. S. pat. 2,590,816 (1952).
¹⁵ W. C. Harden and E. E. Reid, *J. Am. Chem. Soc.*, 54, 4325 (1932).
¹⁶ H. J. Hallowell, U. S. pat. 2,519,565 (1950).
¹⁷ W. C. Harden and J. H. Brewer, *J. Am. Chem. Soc.*, 59, 2379 (1937).
¹⁸ E. C. Kunz and W. S. Gump, U. S. pat. 2,535,077 (1950).
¹⁹ D. M. Musser, U. S. pat. 2,574,189 (1951).
²⁰ L. Givaudan and Cie, Swiss pat. 223,543 (1942).
²¹ M. Luthy and W. S. Gump, U. S. pat. 2,435,593 (1948).
²² C. L. Moyle and P. A. Wolf, U. S. pat. 2,630,458 (1953).
²³ D. E. Cooper and L. C. Cheney, U. S. pat. 2,632,775 (1953).
²⁴ H. J. Florestano, *J. Pharmacol.*, 96, 238 (1948).
²⁵ E. E. Reid and E. Wilson, *J. Am. Chem. Soc.*, 66, 967 (1944).
²⁶ H. E. Faith, U. S. pat. 2,586,316 (1952).
²⁷ A. J. Dietzler and F. Bryner, U. S. pat. 2,503,196 (1950).
²⁸ R. Baltzly, J. S. Buck, E. J. DeBeer, and F. J. Webb, *J. Am. Chem. Soc.*, 71, 1301 (1949).
²⁹ J. E. Johnson and D. R. Mussel, U. S. pat. 2,535,015 (1950).
³⁰ F. D. Snell and K. W. Haeseler, U. S. pat. 2,409,718 (1946).
³¹ M. DeGroote and B. Keiser, U. S. pat. 2,499,361 (1950).
³² H. L. Bock and J. L. Rainey, U. S. pat. 2,504,064 (1950).
³³ P. B. Marsh and M. L. Butler, *Ind. Eng. Chem.*, 38, 701 (1946).
³⁴ L. Haskellberg and D. Lavie, *J. Org. Chem.*, 14, 498-503 (1949).
³⁵ G. T. Bottger and A. P. Yerington, *U. S. Dept. Agr., Bur. Entomol. Plant Quarantine*, E744, 14 (1948).
³⁶ H. M. Day and R. L. DeHoff, U. S. pat. 2,522,569 (1950).
³⁷ R. B. Croad, *J. Soc. Chem. Ind.*, 42, 203T (1923).
³⁸ R. H. Runk, *Ind. Eng. Chem.*, 42, 2110 (1950).
³⁹ S. Robbins and R. H. Runk, *Preprint*, Div. of Paint, Varnish and Plastics Chem., American Chemical Society Meeting, Atlantic City, 1952, p. 88.
⁴⁰ P. Castan, U. S. pat. 2,324,483 (1948).
⁴¹ P. Castan, U. S. pat. 2,444,333 (1948).
⁴² S. O. Greenlee, U. S. pat. 2,494,295 (1950).
⁴³ A. Baeyer, *Ber.*, 5, 25-26 (1872).
⁴⁴ A. Baeyer, *Ber.*, 5, 280-282 (1872).
⁴⁵ J. Scheiber and R. Barthel, *J. prakt. Chem.*, 147, 99-109 (1936).
⁴⁶ R. Barthel, Dissertation, Leipzig, 1936.

- ⁴⁷ T. S. Carswell, *Phenoplasts. Their Structure, Properties and Chemical Technology*, Interscience Publishers, New York, 1947, pp. 6-54.
- ⁴⁸ A. Zinke, *J. Applied Chem.*, **1**, 257-266 (1951).
- ⁴⁹ E. Ziegler, *Oesterr. Chem. Ztg.*, **49**, 92-102 (1948).
- ⁵⁰ E. Ziegler and I. Simmler, *Ber.*, **74B**, 1871-1879 (1941).
- ⁵¹ E. Ziegler and G. Zigeuner, *Kunststoffe*, **39**, 191-192 (1949).
- ⁵² E. Ziegler, *Monatsh.*, **79**, 142-147 (1948).
- ⁵³ R. Wegler and K. Faber, *Ber.*, **82**, 327 (1949); R. Wegler and E. Regel, *Makromolekulare Chem.*, **9**, 1 (1952).
- ⁵⁴ H. von Euler and S. V. deKispeczy, *Z. physik. Chem.*, **A189**, 109 (1941).
- ⁵⁵ A. Vanscheidt, *Org. Chem. Ind. U.S.S.R.*, **3**, 385-393 (1937).
- ⁵⁶ J. B. Fishman, *J. Am. Chem. Soc.*, **42**, 2297-2302 (1920); **42**, 2288-2297 (1920).
- ⁵⁷ H. L. Bender, private communication.
- ⁵⁸ L. H. Baekeland, *J. Ind. Eng. Chem.*, **4**, 737-743 (1912).
- ^{59a} S. R. Finn, J. W. James, and C. J. S. Standen, *Chemistry & Industry*, Feb. 13, 1954, p. 188.
- ^{59b} M. P. Balfe and W. C. Webber, *J. Chem. Soc.*, 1942, 718.
- ^{59c} J. Reese, *Angew. Chem.*, **66**, No. 6, 170-173 (1954).
- ^{59d} J. Reese, *Kunststoffe*, **45**, No. 4, 137-145 (1955).
- ⁶⁰ A. Porai-Koschutz, N. Kudryanzeff, and B. Maschkileison, *Kunststoffe*, **23**, 97-100 (1933).
- ^{60a} J. H. Freeman, private communication.
- ⁶¹ I. P. Losev and M. S. Akutin, *J. Applied Chem. U.S.S.R.*, **13**, 916-925 (1940).
- ⁶² Th. Zincke, *Ann.*, **363**, 246 (1908).
- ⁶³ C. F. Bohringer und Sohne, Ger. pats. 107,720 and 115,817 (1901).
- ⁶⁴ J. Schwyzer, *Chem. Ztg.*, **54**, 817,839 (1930).
- ⁶⁵ A. Gugyot and A. Gry, *Bull. soc. chim. France*, (4) **7**, 902 (1910).
- ⁶⁶ E. Ziegler, *Ber.*, **77**, 731-735 (1944).
- ⁶⁷ D. C. Pepper, *Chemistry & Industry*, 1941, 866.
- ⁶⁸ H. S. Lilley, *J. Soc. Chem. Ind.*, **67**, 196-199 (1948).
- ⁶⁹ K. Hultsch, *Angew. Chem.*, **A60**, 179-184 (1948).
- ⁷⁰ K. Hultsch, *Chemie der Phenolharze*, Springer Verlag., Berlin, 1950.
- ⁷¹ E. Liebnitz and K. Naumann, *Chem. Techn. (Berlin)*, **3**, 5-10 (1951).
- ⁷² E. G. K. Pritchett, *Chemistry & Industry*, 1949, 295-299.
- ⁷³ T. T. Jones, *J. Soc. Chem. Ind.*, **65**, No. 9, 264-275 (1946).
- ⁷⁴ H. Kakiuchi, *Chem. High Polymers (Japan)*, **8**, 29-33 (1951).
- ⁷⁵ E. Imoto and T. Kimura, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **53**, 9-11 (1950).
- ⁷⁶ H. Kakiuchi, *Chem. High Polymers (Japan)*, **8**, 33-43 (1951).
- ⁷⁷ M. Koebner, *Brit. Plastics*, **11**, 7-9, 43 (1939).
- ⁷⁸ M. Koebner, *Brit. Plastics*, **14**, 95-101 (1942).
- ⁷⁹ E. Noelting and W. Herzberg, *Chem. Ztg.*, **16**, 185 (1892).
- ⁸⁰ S. R. Finn, G. J. Lewis, and N. J. L. Megson, *J. Soc. Chem. Ind.*, **69**, Supp. 2, S51-53 (1950).
- ⁸¹ H. L. Bender, A. G. Farnham, and J. W. Guyer, U. S. pat. 2,464,207 (1950).
- ⁸² Trautenberg, *Z. angew Chem.*, **36**, 515 (1923).
- ⁸³ N. J. L. Megson and A. A. Drummond, *J. Soc. Chem. Ind.*, 251-257T (1930).
- ⁸⁴ G. T. Morgan, *J. Soc. Chem. Ind.*, **49**, 206, 245-251T (1930).
- ⁸⁵ F. Seebach, *Kunststoffe*, **27**, 287-290 (1937).

- ⁸⁸ H. Stager and J. Biert, *Helv. Chim. Acta*, **21**, 641-650 (1938).
- ⁸⁷ H. L. Bender and A. G. Farnham, U. S. pat. 2,475,587 (1949); Bakelite Ltd., Brit. pat. 592,278 (1947); Brit. pat. 613,016 (1947).
- ⁸⁸ H. L. Bender, *Modern Plastics*, February, 1953, p. 136.
- ⁸⁹ S. R. Finn and J. W. G. Musty, *J. Soc. Chem. Ind.*, S49-51 (1950).
- ⁹⁰ C. Eberhardt and Ad. Welter, *Ber.*, **27**, 1804 (1895).
- ⁹¹ M. Koebner, *Z. angew. Chem.*, **46**, 251-256 (1933).
- ⁹² G. T. Morgan and N. J. L. Megson, *J. Soc. Chem. Ind.*, **52**, 418-420T (1933).
- ⁹³ S. R. Finn, *J. Soc. Chem. Ind.*, **69**, Supp. 1, 57-59 (1950).
- ⁹⁴ S. R. Finn, N. J. L. Megson, and E. J. W. Whittaker, *Chemistry & Industry*, S849-853 (1950).
- ⁹⁵ N. J. L. Megson, *J. Soc. Chem. Ind.*, **52**, 420-424T (1933).
- ⁹⁶ Chattaway and Goepp, *J. Chem. Soc.*, 1933, 699.
- ⁹⁷ N. Caro, *Ber.*, **25**, 939-949 (1892).
- ⁹⁸ E. Clemmensen and A. H. C. Heitman, *J. Am. Chem. Soc.*, **33**, 737 (1911).
- ⁹⁹ E. H. Madsen, *Arch. Pharm.*, **245**, 42-48 (1907).
- ¹⁰⁰ R. Möhlau and P. Koch, *Ber.*, **27**, 2888 (1894).
- ¹⁰¹ R. Boehm, *Ann.*, **329**, 270-272 (1903).
- ¹⁰² R. Fabinyi, *Ber.*, **9**, 283-286 (1878).
- ¹⁰³ A. Claus and E. Trainer, *Ber.*, **19**, 3004-3011 (1886).
- ¹⁰⁴ L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, **17**, 225-237 (1925).
- ¹⁰⁵ A. Lunjak, *J. Russ. Phys. Chem. Soc.*, **36**, 301-311 (1904).
- ¹⁰⁶ J. B. Niederl and J. S. McCoy, *J. Am. Chem. Soc.*, **63**, 1731 (1941).
- ¹⁰⁷ E. Adler, H. von Euler, and G. J. Gie, *Arkiv Kemi Mineral. Geol.*, **A16**, No. 12, 1-20 (1943).
- ¹⁰⁸ J. C. Ambelang and J. L. Binder, *J. Am. Chem. Soc.*, **75**, 947 (1953).
- ¹⁰⁹ H. Pauly and A. Schanz, *Ber.*, **56**, 979 (1923).
- ¹¹⁰ K. Elbs, *J. prakt. Chem.*, (2), **47**, 60 (1893).
- ¹¹¹ Edm. ter Meer, *Ber.*, **7**, 1200 (1874).
- ¹¹² K. Elbs and D. Hörmann, *J. prakt. Chem.*, (2), **39**, 498 (1899).
- ¹¹³ L. Haskelberg and D. Lavie, *J. Org. Chem.*, **14**, 498-503 (1949).
- ¹¹⁴ F. D. Chattaway and F. Calvert, *J. Chem. Soc.*, 1928, 1088-1094.
- ¹¹⁵ F. D. Chattaway and A. A. Morris, *J. Chem. Soc.*, 1927, 2013-2017.
- ¹¹⁶ F. D. Chattaway and F. Calvert, *J. Chem. Soc.*, 1927, 685.
- ¹¹⁷ F. D. Chattaway, *J. Chem. Soc.*, 1926, 2720-2727.
- ¹¹⁸ R. N. Sen and N. N. Sinha, *J. Am. Chem. Soc.*, **45**, 2984-2996 (1923).
- ^{118a} J. E. Driver and J. B. Sousa, *J. Chem. Soc.*, 1954, 985-989.
- ¹¹⁹ C. Moureau and C. Dufraisse, Ger. pat. 382,903 (1920).
- ¹²⁰ J. McIntosh, *Ind. Eng. Chem.*, **19**, 111 (1927).
- ¹²¹ B. V. Maksorow and K. A. Andrianow, *Ind. Eng. Chem.*, **24**, 827-833 (1932).
- ¹²² E. Adler and S. Tingstam, *Arkiv Kemi Mineral. Geol.*, **B16**, No. 18, 1-7 (1943).
- ¹²³ J. E. Jansen, U. S. pat. 2,468,982 (1949).
- ¹²⁴ A. J. Dietzler, U. S. pat. 2,526,545 (1950).
- ¹²⁵ C. G. Schwarzer, S. Ballard, and D. B. Luten, U. S. pat. 2,602,821 (1952).
- ¹²⁶ J. A. Arvin, U. S. pat. 1,986,423 (1935).
- ¹²⁷ A. Dianin, *J. Russ. Phys. Chem. Ges.*, **1**, 488,523,601 (1891); A. Dianin, *Ber.*, **25**, 334R (1892).
- ¹²⁸ N. D. Coggeshall, *J. Am. Chem. Soc.*, **72**, 2836 (1950).
- ^{128a} G. R. Sprengling, *J. Am. Chem. Soc.*, **76**, 1190 (1954).

- 129 K. Fries and K. Kann, *Ann.*, **353**, 335-356 (1907).
- 130 A. Zinke and E. Ziegler, *Ber.*, **74**, 541-545 (1941).
- 131 K. Auwers, *Ber.*, **50**, 2524 (1907).
- 132 F. S. Granger, *Ind. Eng. Chem.*, **29**, 1305-1308 (1937).
- 133 R. Barthel, *Plastica (Holland)*, **2**, 247-251 (1949).
- 134 R. W. Martin, *J. Am. Chem. Soc.*, **73**, 3952-3954 (1951); U. S. pat. 2,579,329 (1951).
- 135 J. H. Freeman and C. W. Lewis, *J. Am. Chem. Soc.*, **76**, 2080-2087 (1954).
- 136 J. B. Niederl and I. W. Ruderman, *J. Am. Chem. Soc.*, **67**, 1176-1178 (1945).
- 137 E. Ziegler, I. Hontschik and L. Milowiz, *Monatsh.*, **78**, 334 (1948).
- 138 J. B. Niederl and J. S. McCoy, *J. Am. Chem. Soc.*, **65**, 629-631 (1943).
- 139 *Technical Bulletin on Dimethylaminomethylphenols*, Rohm and Haas Co.
- 140 A. Reyckler, *Bull. soc. chim. France*, **1**, 1195 (1907).
- 141 J. Breslau and A. Pictet, *Ber.*, **40**, 3785 (1907).
- 142 R. W. Martin, unpublished work.
- 143 L. Claisen, *Ann.*, **237**, 270 (1887).
- 144 H. von Euler, E. Adler, and J. O. Cedwall, *Arkiv Kemi Mineral. Geol.*, **15A**, No. 19, 1-10 (1942).
- 145 J. W. LeMaistre and R. B. Seymour, *J. Am. Chem. Soc.*, **70**, 1776 (1948).
- 146 C. S. Marvel, R. J. Gander, and R. R. Chambers, *J. Poly. Sci.*, **4**, 689-702 (1949).
- 147 G. E. P. Smith, Jr., J. C. Ambelang, and G. W. Gottschalk, *Ind. Eng. Chem.*, **38**, 1166 (1946).
- 148 H. L. Bender, *Mod. Plastics*, February, 1953, pp. 136-138, 220-222; March, 1954, pp. 115-118, 200.
- 149 K. Auwers and E. Rietz, *Ann.*, **356**, 152-177 (1908).
- 150 N. J. L. Megson, *J. Soc. Chem. Ind.*, **58**, 131-139 (1939).
- 151 J. Strating and H. J. Backer, *Rec. trav. chim.*, **62**, 57 (1943).
- 152 G. T. Morgan and N. J. L. Megson, *J. Soc. Chem. Ind.*, **52**, 418-420T (1933).
- 153 K. Auwers, *Ber.*, **36**, 1878 (1903).
- 154 Ng. Ph. Buu-Hoi, Denise Lavit, and Ng. D. Xuong, *J. Chem. Soc.*, **1953**, 2612.
- 155 H. von Euler, E. Adler, and J. O. Cedwall, *Arkiv Kemi Mineral. Geol.*, **A14**, No. 14A, 1-20 (1941).
- 156 K. Auwers, *Ber.*, **40**, 2524-2537 (1907).
- 157 E. Adler, H. von Euler, and J. O. Cedwall, *Arkiv Kemi Mineral. Geol.*, **A15**, No. 7, 1-17 (1941).
- 158 K. Auwers, *Ann.*, **344**, 271, 284 (1906).
- 159 S. R. Finn and J. W. G. Musty, *J. Soc. Chem. Ind.*, Supp. Issue I, S3-7 (1950).
- 160 G. Zigeuner, E. Ziegler, W. Schaden, and W. Weisenberger, *Monatsh.*, **81**, 326-329 (1950).
- 161 A. Buroway and J. T. Chamberlain, *J. Chem. Soc.*, **1949**, 624-626.
- 162 H. von Euler and G. Holmberg, *Kunststoff-Tech. u. Kunststoff-Anwend.*, **10**, 62 (1940).
- 163 K. Hultsch, *J. prakt. Chem.*, **159**, 155-179 (1941).
- 164 C. A. Buehler, D. E. Cooper, and E. O. Scrudder, *J. Org. Chem.*, **8**, 316 (1943).
- 165 W. S. Gump and M. Luthy, U. S. pat. 2,344,408 (1943).
- 166 C. A. Buehler, R. L. Brown, J. M. Holbert, J. G. Fulmer, and G. W. Parker, *J. Org. Chem.*, **6**, 902-907 (1941).

- ¹⁶⁷ A. Zincke, F. Hanus, and E. Ziegler, *J. prakt. Chem.*, (2), **152**, 126-144 (1939).
¹⁶⁸ G. Zigeuner and E. Wiesenberger, *Monatsh.*, **80**, 801-811 (1949).
¹⁶⁹ Zincke and Birschel, *Ann.*, **362**, 237 (1908).
¹⁷⁰ A. T. Carpenter and R. F. Hunter, *J. Applied Chem.*, **1**, Pt. 5, 217-226 (1951).
¹⁷¹ K. Auwers, *Ann.*, **343**, 171-192 (1905).
¹⁷² M. Kohn and M. Jawetz, *Monatsh.*, **44**, 198 (1923).
¹⁷³ K. Auwers and C. Kipke, *Ann.*, **344**, 194-226 (1905).
¹⁷⁴ M. Kohn and M. Jawetz, *Monatsh.*, **45**, 251 (1924).
¹⁷⁵ E. Adler, S. Tingstam, and A. O. Caspersson, *Arkiv Kemi Mineral Geol.*, **B15**, No. 10, 1-8 (1942).
¹⁷⁶ M. M. Sprung and M. T. Gladstone, *J. Am. Chem. Soc.*, **71**, 2907-2913 (1949).
¹⁷⁷ H. von Euler, E. Adler, S. deKispeczy, and A. Fagerlund, *Arkiv Kemi Mineral. Geol.*, **A14**, No. 10, 1-20 (1940).
¹⁷⁸ E. Ziegler and K. Gartler, *Monatsh.*, **80**, 634-639 (1949).
¹⁷⁹ E. Ziegler, G. Zigeuner, and A. Kainzner, *Monatsh.*, **80**, 295-302 (1949).
¹⁸⁰ E. Adler and S. Kyrning, *Svensk Kem. Tid.*, **53**, No. 1, 5-11 (1940).
¹⁸¹ H. V. Euler, E. Adler, and D. Friedman, *Arkiv Kemi Mineral. Geol.*, **B13**, No. 12, 1-7, (1939).
¹⁸² A. Steiner, *Ber.*, **9**, 287-289 (1878).
¹⁸³ V. Ettel and J. Weichet, *Collection Czechoslov. Chem. Commun.*, **13**, 433-441 (1948).
¹⁸⁴ Th. Zincke and M. Grueters, *Ann.*, **343**, 75-99 (1905).
¹⁸⁵ M. E. McGreal, V. Niederl, and J. B. Niederl, *J. Am. Chem. Soc.*, **61**, 345-348 (1939).
¹⁸⁶ J. C. Sheehan and G. D. Laubach, *J. Am. Chem. Soc.*, **72**, 2478-2481 (1950).
¹⁸⁷ K. Shishido, H. Nozaki, and T. Iwako, *J. Am. Chem. Soc.*, **71**, 2037-2071 (1949).
¹⁸⁸ E. Adler, H. von Euler, and C. J. Gie, *Arkiv Kemi Mineral. Geol.*, **A18**, No. 1, 1-21 (1944).
¹⁸⁹ K. Sisido, H. Nozaki, and O. Kurihara, *J. Am. Chem. Soc.*, **72**, 2270-2272 (1950).
¹⁹⁰ J. B. Niederl and R. N. Nagel, *J. Am. Chem. Soc.*, **63**, 1235-1237 (1941).
¹⁹¹ A. R. Bader and A. D. Kontowicz, *J. Am. Chem. Soc.*, **76**, 4465 (1954).
¹⁹² C. L. Moyle and P. A. Wolf, U. S. pat. 2,612,932 (1952).
¹⁹³ J. W. Churchill, U. S. pat. 2,698,866 (1955).

C H A P T E R F O U R

Phenolic Resins

Phenolic resins are of two main types. The resins resemble either the phenol alcohols or the dihydroxydiphenylalkanes in basic structure. If they are prepared with an excess of formaldehyde and an alkaline catalyst they will resemble the phenol alcohols and have methylol side or end groups. Such resins are often referred to as resoles. They are capable of being cured by the application of heat and acids, cure resulting through condensation of the methylol groups. By cooling the resin the reactions may be conveniently stopped, or at least effectively retarded, anywhere between the addition of the formaldehyde and the final curing process. To resume reaction the temperature is raised or an acidic catalyst is added. Since there is no sharp break in these reactions such resins have been termed the One-Stage resins. The majority of the One-Stage resins employ formaldehyde as the aldehyde, although certain other aldehydes may be used.¹⁻³ Formaldehyde is preferred because of its high reactivity and freedom from side reactions.

On the other hand, if the phenolic resin is prepared with an acidic catalyst and less than a mole of formaldehyde per mole of phenol the resin will resemble a dihydroxydiphenylmethane in structure, e.g. the chains are phenol ended. These resins, commonly referred to as novolacs,* are permanently soluble and fusible and cure only upon the addition of a curing agent. As the preparation of the novolac resin represents one process and the addition of the curing agent represents a separate and distinct process, resins based on a novolac resin and a curing agent are referred to as Two-Stage resins. An outline of the two processes is given in Fig. 2. For clarity of treatment the preparation and properties of the novolac resins and of the resoles will be considered separately.

A rather detailed outline of the development of phenolic resins from a historical point of view has been given by several authors.⁴⁻⁷

* At one time trademarked as "Novolak."

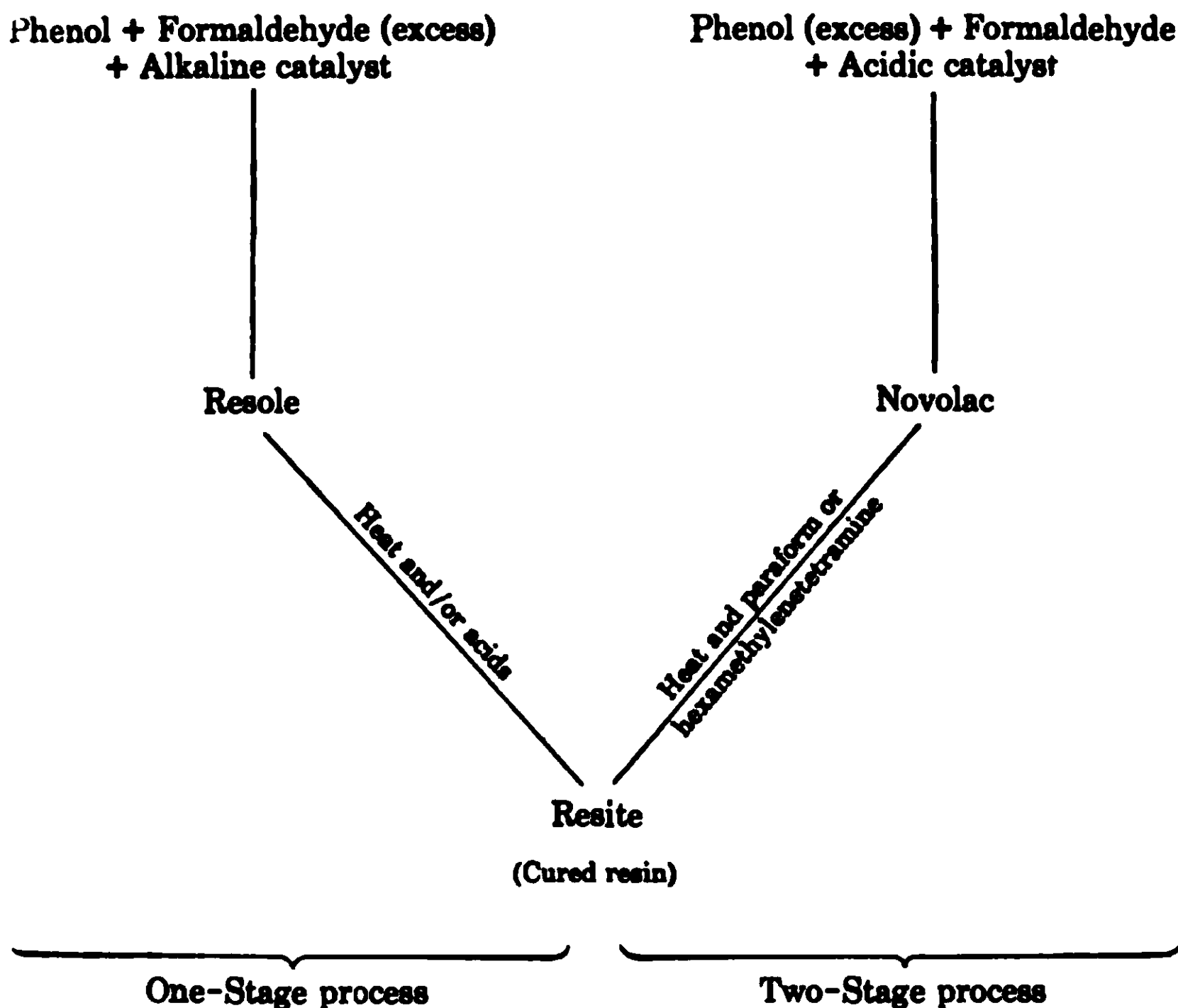


Fig. 2. Phenolic resin processes.

RESOLES

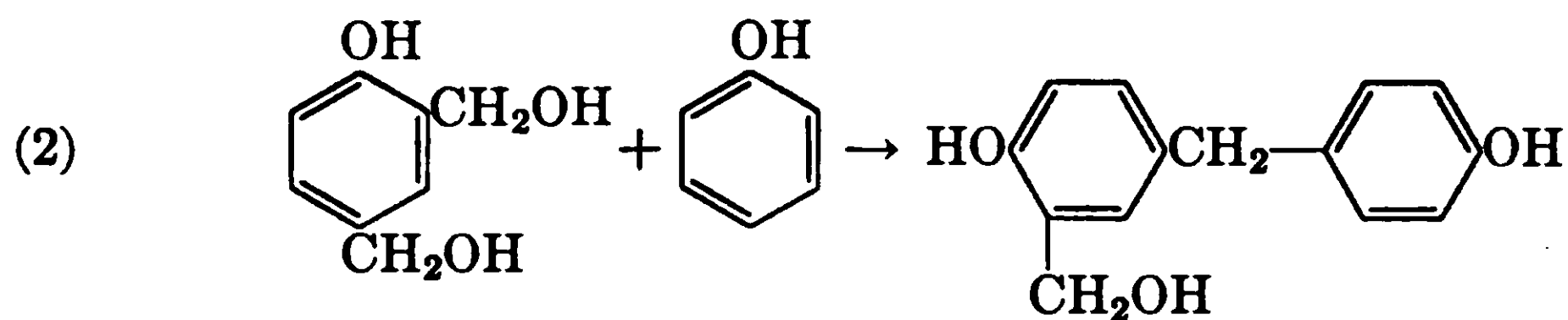
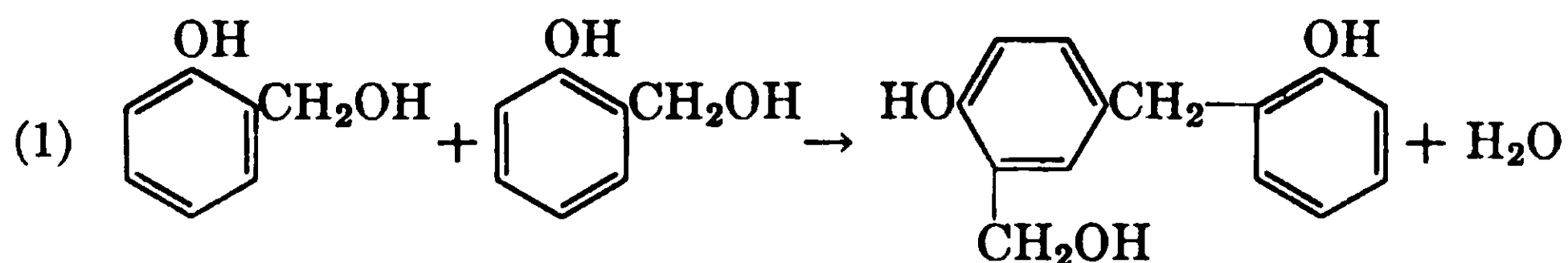
The initial phenol-aldehyde condensation products obtained with alkaline catalysts were named "resoles" by Lebach;⁸⁻¹⁰ they correspond to the soluble and fusible A stage resins as defined by Baeke-land.^{5,11,12} Chemically, resoles are a complex mixture of mono- and polynuclear phenolic bodies possessing reactive methylol groups, the polynuclear compounds being derived from the simpler mononuclear phenol alcohols.¹⁸⁻¹⁹ The exact nature of the linkages in the more complex resole molecules and their mode of formation are among the most interesting aspects of the chemistry of phenolic resins.

It has been suggested that the nuclei of the polynuclear bodies in a resole may be joined by way of dibenzyl ether linkages, but there is little evidence to indicate that dibenzyl ether formation is an important reaction under alkaline conditions as found during resole manufacture. However, dibenzyl ethers play an important part in the cure of a resole under neutral conditions and they may be involved to some extent under acidic conditions as well. Sprung and Gladstone²⁰ found that saligenin readily formed 2,2-dihydroxydibenzyl ether when heated alone, but the ether was not detected when the reaction was carried out in the presence of alkali. Reese,^{20a} in a detailed study of

the condensation of *o*- and *p*-methylophenol, 2,4- and 2,6-dimethylophenol, and trimethylophenol, later found that none of the compounds formed dibenzyl ether derivatives under alkaline conditions. Zinke and Ziegler²¹ also have shown that alkali catalyzes the formation of dihydroxydiphenylmethanes from dibenzyl ethers. These data indicate that even if formed most dibenzyl ethers would be converted to methylene bridges in the presence of alkali. Actually only one example of dibenzyl ether formation under alkaline conditions was found in the literature.²² This single example involved the reaction of the negatively substituted *o*-bromo-*p*-cresol with formaldehyde.

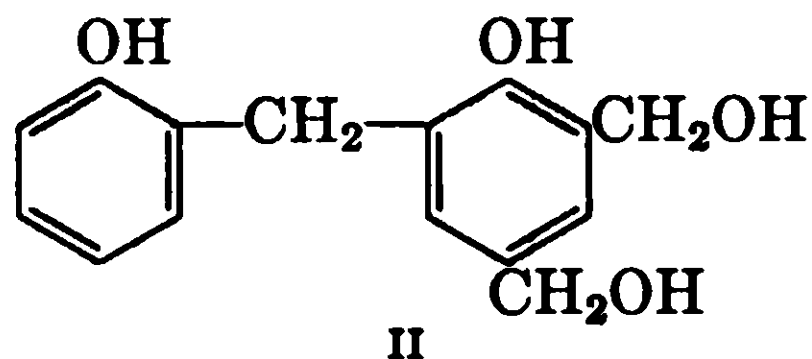
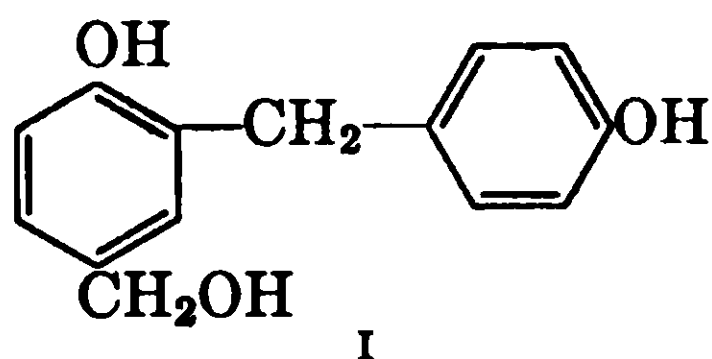
Lilley²³ has examined the possibility of ether formation as compared to methylene bridge formation on the basis of purely theoretical considerations. He concluded that dibenzyl ethers can only be formed within certain limited and critical pH ranges. These ranges do not coincide with common technological practice for the preparation of resoles.

A far more important means than ether linkages for tying phenol alcohols together is by methylene bridges. Many of the early workers were aware of the importance of this reaction.^{16, 24-27} Reaction could occur by condensation of a methylol group of a phenol alcohol and an *ortho* or *para* hydrogen of another phenol alcohol molecule or even with unreacted phenol, equations 1 and 2.



As can be seen from these equations, if two phenol alcohols or a phenol polyalcohol and an equal molar quantity of phenol are condensed, the products will carry a methylol group. Only by condensation of a phenol monoalcohol with free phenol would a dihydroxydiphenylmethane devoid of methylol groups be obtained, and even this product is still capable of adding methylol groups under the conditions of resole manufacture. Few polymer molecules devoid of methylol groups would be formed in most instances. Accordingly, a

resole would be a complex mixture of mono- and polynuclear phenol alcohols in which the phenol nuclei of the latter would be joined by methylene bridges. Carpenter and Hunter²⁸ and Finn, James, and Standen²⁹ have succeeded in preparing some typical polynuclear phenol alcohols, examples of which are shown below, I and II.

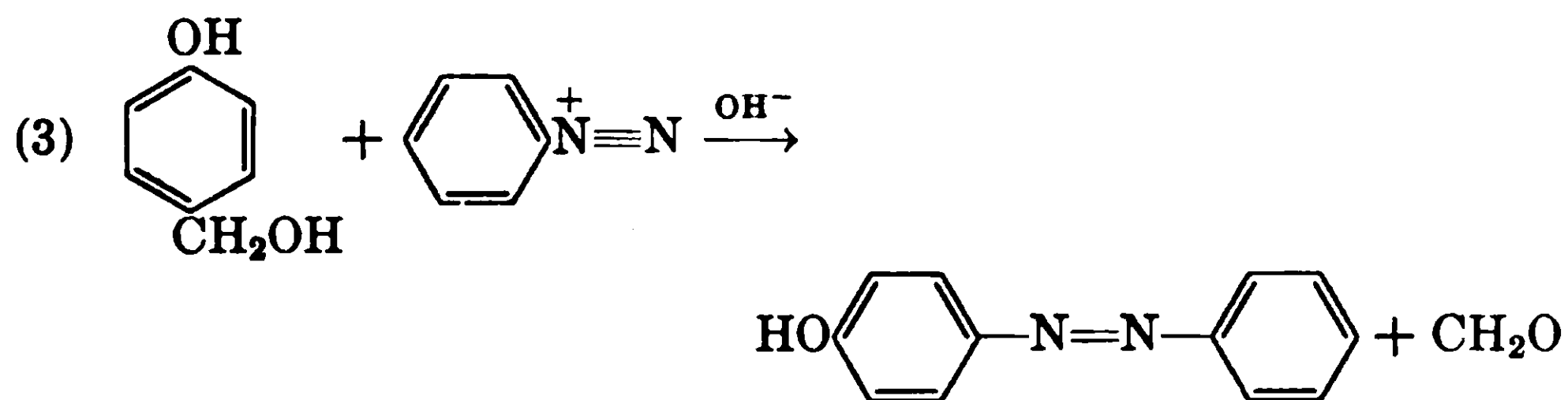


It was generally assumed by the early workers that the methylene bridges were formed exclusively, as shown in equations 1 and 2, by the elimination of water between a methylol group from one phenolic body and an *ortho* or *para* hydrogen of another phenolic body. Such reactions occur under a wide range of conditions and are undoubtedly responsible for an important part of the condensations that occur during resole manufacture. However, other means exist for the formation of a methylene bridge.

It was found soon after the turn of the century, and has been confirmed by many workers since then, that phenol alcohols such as the monoalcohols of 2,4- and 2,6-xyleneol form dihydroxydiphenylmethanes and eliminate formaldehyde on heating with alkalis.^{15,21,30-32}

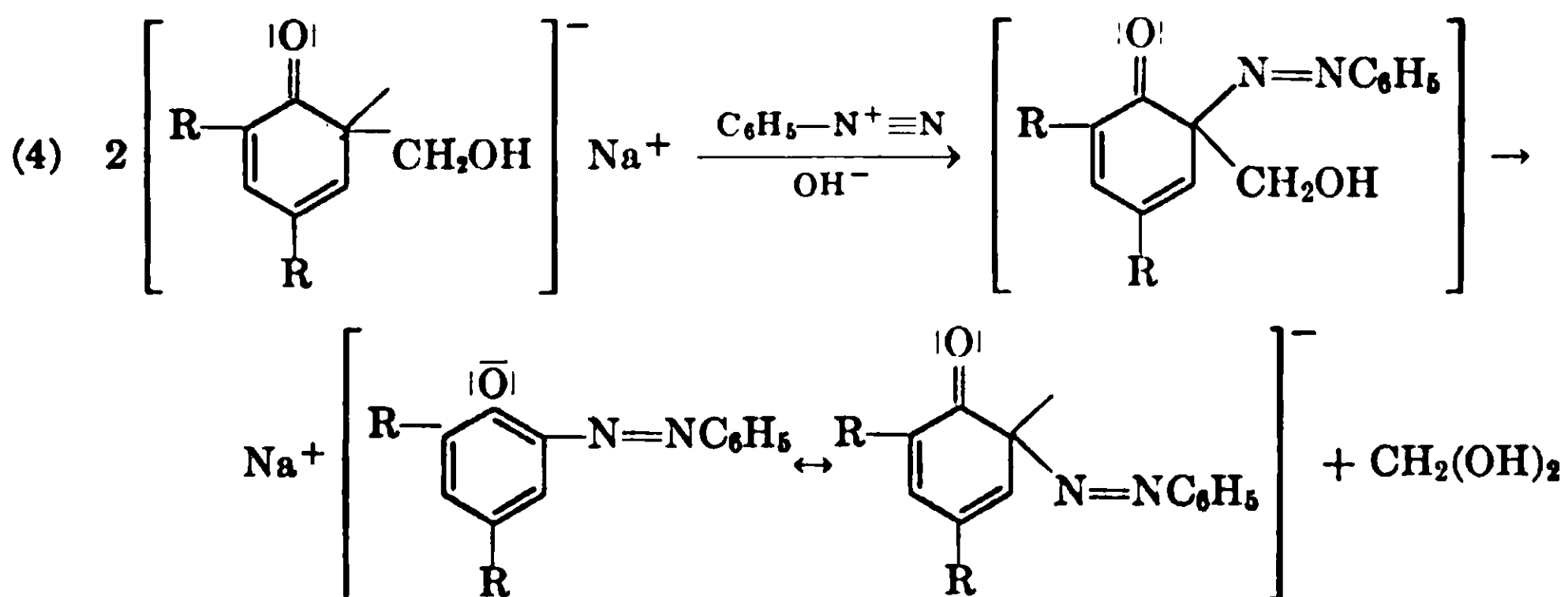
At first the reaction involving the elimination of formaldehyde from two molecules of a phenol alcohol was assumed to occur only with phenol alcohols with no free reactive positions. Experiments by Ziegler and Zigeuner¹⁷ and Barthel³³ indicate that this type of reaction may not be unique to blocked phenols. Barthel found that the addition of phenols having free reactive positions to certain phenol alcohols in alkaline solution had no appreciable effect on the yield of dihydroxydiphenylmethane obtained. Ziegler and Zigeuner obtained similar results with 2-hydroxy-3,5-dimethylbenzyl alcohol, and Freeman and Lewis³⁴ found that the addition of 2,6-dimethylolphenol to a solution of 2,4,6-trimethylolphenol in alkali actually retarded the formation of tetramethyldihydroxydiphenylmethane. These findings suggested that the phenol alcohols were reacting only with themselves since the addition of phenols with reactive positions on the ring did not accelerate the reaction. It indicated further that under alkaline conditions a position occupied by a methylol group may be more reactive towards another methylol group than towards a free *ortho* or *para* hydrogen of a phenol.

Data in another field were published about the same time by Ziegler and Zigeuner which have an important bearing on the problem.^{17, 33, 35-37} (See also ref. 38.) These authors studied the reactions of phenol alcohols with diazonium compounds under alkaline conditions. They found that diazonium compounds may react with phenol alcohols by displacement of a methylol group with an azobenzene group and liberate free formaldehyde, equation 3. The displacement



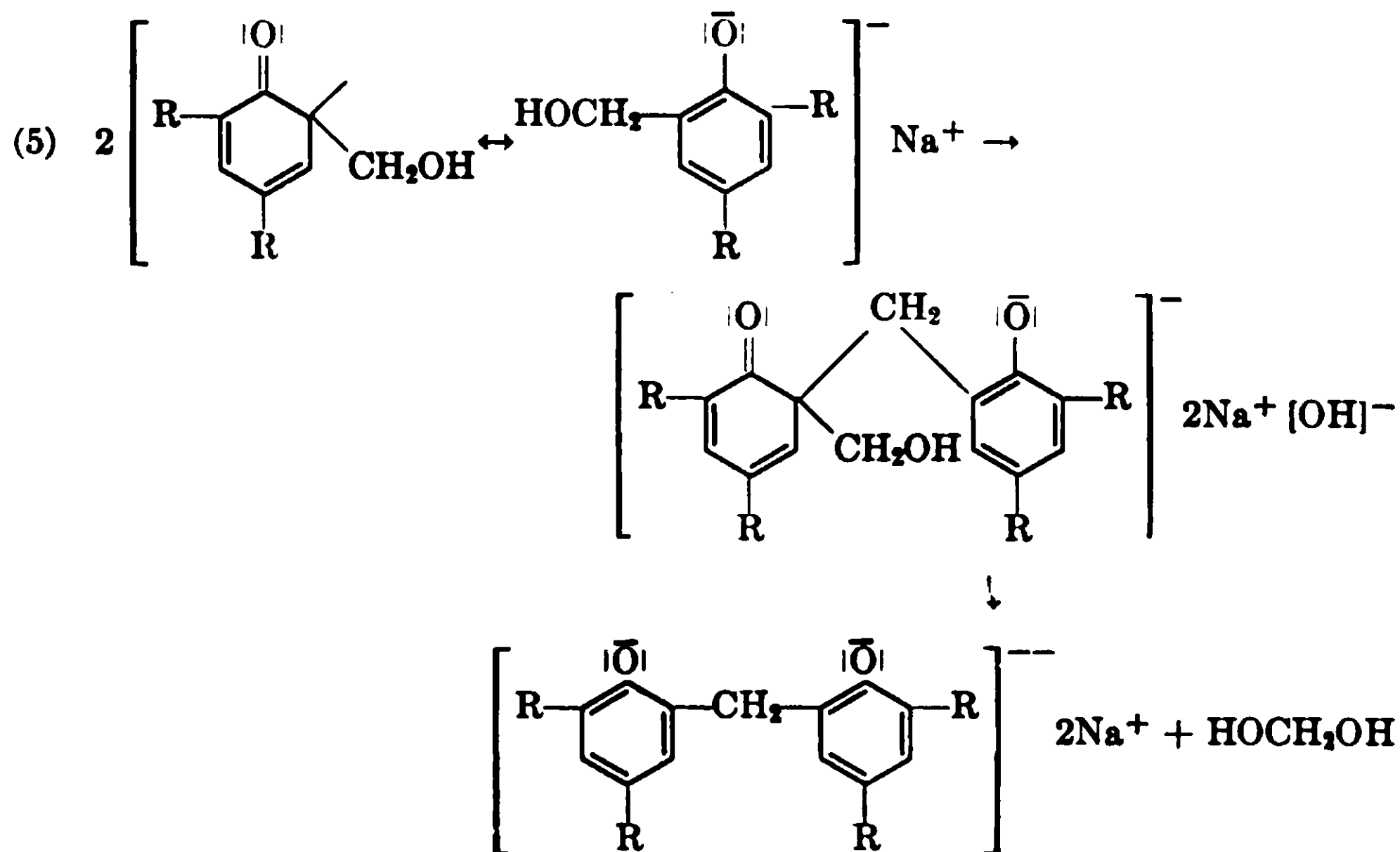
of a methylol group often occurred even when free positions were available on the phenol alcohol for coupling with the diazonium compound. A more detailed study of the reaction revealed that displacement of a methylol group or coupling at a free position was controlled by the location of the methylol group. Ziegler concluded that in general (some exceptions were found) replacement of a *p*-methylol group occurs preferentially, followed by replacement of a *p*-hydrogen, replacement of an *o*-methylol group, and finally replacement of an *o*-hydrogen. Freeman³⁹ claims that Ziegler is correct concerning the order of reaction at an *o*-position but is incorrect concerning the *p*-position where a *p*-hydrogen is replaced preferentially to a *p*-methylol group.

Since the reaction with the diazonium compounds occurs at room temperature and the rate approaches that of an ionic reaction, an ionic type of mechanism has been proposed by Ziegler and Zigeuner, equation 4.



The interest in the work with the diazonium compounds stems from the fact that the reactions of a phenol alcohol with diazonium compounds or with another phenol appear to have certain similarities. More detailed studies, particularly of the phenol alcohols, are needed to establish how far the analogy goes. The limited data now available indicate that, in both reactions, displacement of a methylol group from certain phenol alcohols occurs more readily under alkaline conditions than displacement of a ring hydrogen. Unsubstituted or negatively substituted phenol alcohols, which yield dihydroxydiphenylmethanes with difficulty, or not at all, under alkaline conditions, also react poorly, or not at all, with diazonium compounds. Saligenin, for example, reacts sluggishly, and 2,4-dichloro-6-hydroxymethylphenol and 2,4-dibromo-6-hydroxymethylphenol fail to react with diazonium salts. These same phenol alcohols show exceptional stability in an alkaline medium and may be boiled for several hours with little or no change. On the other hand phenol alcohols, such as those derived from 2,6-xylenol, which readily form dihydroxydiphenylmethanes in an alkaline medium, couple with ease with diazonium compounds.

Since the two reactions appear to be similar, Ziegler and Zigeuner¹⁷ think that the mechanism for the two reactions should also be analogous and have given the mechanism, equation 5, for the formation of dihydroxydiphenylmethanes from phenol alcohols under alkaline con-



ditions. This mechanism is similar to that suggested by Huckel⁴⁰ for the Kolbe and Reimer-Tiemann reactions. The above mechanism

applies only where the displacement of a methylol group is involved.

In resole manufacture, where strong alkalies are used as catalysts, the importance of the theories discussed above become apparent. If the mechanism is shown to be generally applicable to commercial resoles it means that a mole of formaldehyde would be eliminated for each methylene bridge established by this mechanism. The formaldehyde eliminated would then be free to recombine with phenolic bodies in the system. Under such circumstances the progress of both the addition of methylol groups and the formation of methylene bridges becomes difficult to follow. Yet, in the final analysis the relative rates for the two reactions control the composition of a resole. Provided that the discussion is limited to phenol, where the greatest amount of data is available, some tentative proposals may be made as to the interplay of the two reactions and how they affect the composition of a resin.

Before starting to assess what will happen to the intermediate phenol alcohols, once formed, those most likely to be formed and their relative amounts must be known. Freeman and Lewis⁸⁴ have provided much of the information available in this field. Their data were obtained on a reaction run at 30°C. with a mole of caustic and 3 moles of formaldehyde for each mole of phenol. As most commercial resoles are prepared at higher temperatures with less formaldehyde and with much less caustic the findings of Freeman and Lewis may not be strictly applicable to commercial resoles. However, their results provide a starting point for a discussion of the problem.

Freeman and Lewis found that although the *para* position of phenol has a slightly greater affinity for formaldehyde than an *ortho* position the two *ortho* positions overcome this deficiency and saligenin is produced at a greater rate than *p*-hydroxybenzyl alcohol. Saligenin will therefore be the first phenol alcohol to appear in appreciable quantity in a phenol-formaldehyde reaction mixture under their conditions. *p*-Hydroxybenzyl alcohol will appear somewhat later than saligenin, but owing to its low reactivity with formaldehyde its concentration will increase as long as phenol is available in the system. On the other hand, saligenin will react further with formaldehyde at about the same rate as it is formed, and thus its concentration in the reaction mixture will not change rapidly. Because of its low reactivity with formaldehyde, 2,4-dimethylolphenol will accumulate in the system while only traces of the highly reactive 2,6-dimethylolphenol will be found. Trimethylolphenol will become an important constituent of the reaction mixture late in the reaction provided that a fairly high ratio of formaldehyde to phenol is used.

Obviously in a commercial resole where the ratio of formaldehyde to phenol is less than that used by Freeman and Lewis the formation of the higher phenol alcohols will be reduced. Keeping this in mind, something of the structure of a resole may be visualized by knowing how the various phenol alcohols condense with themselves, with each other, and with free phenol. Reese,^{20a} in an excellent series of experiments, has made the most detailed study of this problem. He heated each of the five possible phenol alcohols of phenol in acidic and alkaline solution at 70°C. and in a melt at 110°C. The phenol alcohols were heated alone and in the presence of free phenol under each set of conditions. After a predetermined heating period the products of the reaction were separated by two-dimensional chromatography. By comparing the R_f values of the fractions with the R_f values of known compounds, where available, and by considering the known effects of structure on an R_f value where reference compounds were not available, Reese was able to assign either definitive or highly probable structures to the various fractions separated by chromatography. Since alkalies are the standard catalyst used in preparing resoles, the present discussion will be limited to the results found by Reese where the condensations were carried out under alkaline conditions.

Under alkaline conditions saligenin and 2,6-dimethylolphenol condensed when heated alone to form a methylene derivative by reaction of a methylol group with a free *para* hydrogen on the ring of the phenol alcohol. No loss of formaldehyde was noted. On the other hand, *p*-hydroxybenzyl alcohol, 2,4-dimethylolphenol, and trimethylolphenol all formed methylene derivatives by coupling preferentially at the *para* position. The reactions were accompanied by the loss of water and formaldehyde. Since Freeman and Lewis found that *p*-hydroxybenzyl alcohol and 2,4-dimethylolphenol are likely to accumulate in a resole, at least under their conditions, the importance of the reaction between the methylol groups of these phenol alcohols, which occurs by the elimination of formaldehyde, becomes apparent.

With phenol present during the condensation the formation of methylene bridges by reaction of the *para* hydrogen of the phenol with a methylol group of the phenol alcohol appeared to be a very important reaction, according to Reese. This point is significant since phenol is an important constituent of most resoles. Reaction occurred most readily with a *para* methylol group when both a *para* and an *ortho* methylol group was available. These and other data strongly indicate that *para* methylol groups are very important in building up the polynuclear chains in the higher-molecular-weight resoles. This would mean that most of the methylol groups attached to the higher-

molecular-weight resins will be at an *ortho* position. It would also mean that much of the final cure of resole would be through *ortho* methylol groups.¹⁹

The average number of methylol groups per phenol nucleus of a resole will depend on a variety of factors, including the phenol-formaldehyde ratio, duration and temperature of reaction, type and concentration of catalyst, and the phenol employed. Strong alkalies have a pronounced catalytic effect on the addition of methylol groups. But according to Granger ⁴¹ an increase in the amount of catalyst above a certain point (approximately $\frac{1}{20}$ mole per cent of caustic) has no further effect on the rate of the condensation reaction. Goldblum ⁴² and Sprung ²⁰ have obtained similar results. This rather unusual effect of catalyst coupled with a large temperature coefficient for both the methylation and the condensation reaction makes possible the preparation of resins with an extremely wide range of properties. Resins with very different properties are possible by the combination of phenol and formaldehyde even at a single ratio. When variations in the phenols and in the ratio of the phenol to the formaldehyde are included the possibility for altering the properties of the resins becomes very great.

Some of the effects of reaction conditions on resin properties may be illustrated by use of phenol and formaldehyde at a single ratio, e.g. 1:1.3, with NaOH as a catalyst. At a low temperature and a high concentration of catalyst a product consisting almost entirely of mononuclear phenol alcohols results. The product will be infinitely soluble in water. With less caustic and a short time at reflux temperature a resole which will tolerate dilution with several volumes of water is still possible although it may no longer have infinite water dilutability. However, with low catalyst concentration and particularly after an extended period of reaction at reflux temperature a resole will be obtained which will be composed mainly of polynuclear bodies, soluble only in strong solvents such as acetone. If the condensation is carried too far, solubility in all solvents will be lost.

Bettleheim and Nihlberg ⁴⁸ recognize six distinct steps in resin manufacture: (1) warming-up time; (2) ripening, the time at condensation temperature before the resin starts to precipitate; (3) post ripening, the time the resin is held at condensation temperature after resin separates from the aqueous phase; (4) distillation; (5) concentration, the period the resin is held under vacuum and heated to advance to the desired viscosity; (6) cooling. Bettleheim and Nihlberg strongly emphasize that such properties as viscosity and density alone are not true criteria of the status of a resin or of the behavior to be expected

of the resin. The type of resin obtained depends on the way each of the six steps of the manufacture are handled. If each step in the process is made to follow a set schedule, then, and then only, do the viscosity, refractive index, etc., have any meaning so far as over-all properties of a resin are concerned.

As mentioned earlier, resoles generally contain appreciable quantities of unreacted phenol. This is particularly true for resins prepared with less than 1.5 moles of formaldehyde per mole of phenol. The quantity of unreacted phenol in commercial One-Stage resins may be as high as 20% according to Lewin and Robitschek.⁴⁴ Smith, Rugg, and Bowman⁴⁵ found between 2 and 15% phenol in the resins they examined. The conditions of reaction, at a constant phenol-to-formaldehyde ratio, also have a large effect on this figure, low reaction temperature and strong alkaline catalysts tending to increase the amount of unreacted phenol. Obviously a decrease in the amount of formaldehyde employed per mole of phenol also will increase the amount of unreacted phenol. Vanscheidt⁴⁶ has measured the phenol content of phenol-formaldehyde reaction mixtures as a function of time of reaction, formaldehyde consumption, and catalyst at several phenol-to-formaldehyde ratios.

Water is extremely difficult to remove from One-Stage resins.⁴⁷ This means that most commercial resins, even in the solid form, will contain water. In addition, further quantities of water are eliminated during cure.

By way of summary, it may be stated with a fair degree of certainty that a resole is a complex mixture of mono- and polynuclear phenolic molecules possessing reactive methylol groups. The polynuclear molecules will be joined exclusively by methylene bridges prior to neutralization of the alkaline catalyst. If the resin is condensed further under neutral conditions dibenzyl ether linkages will then be found. Essentially all resins will contain unreacted phenol, and in many the quantity will be appreciable. Completely dehydrated resins will be very difficult, if not impossible, to obtain.

In addition to the above picture of a resole, some insight into the proportions of the various constituents has been obtained by fractional precipitation and similar studies.^{18, 48-50} Vanscheidt^{46, 51, 52} and Müller and Müller⁵³ in particular have been very active in studying the composition of alkali-catalyzed resins. It is interesting to note that Müller and Müller have found that during the early and intermediate stages of condensation the amount of low-molecular-weight material in a resin remains about constant while the amount of high polymer increases as the condensation is continued.

Manufacture of Resoles

Each manufacturer of phenolic resins usually supplies to the trade a variety of resins, each designed for a particular end use. For each, the conditions of manufacture have been worked out in detail, and there are undoubtedly hundreds of different resins now in use. However, it may be of interest to describe briefly a typical process for the manufacture of some of the more common resoles or One-Stage resins.

Water-Soluble Resin. For each mole of phenol, 1.25–1.35 moles of formaldehyde as formalin solution is used. The reaction is catalyzed by addition of 20–25 ml. of 3–4 *N* sodium hydroxide. The reaction mixture is refluxed for 40–45 minutes. If the resin is to be partially dehydrated the reaction period may have to be shortened and the dehydration conducted at a very low temperature; otherwise, water solubility will be lost. Resin formation can be essentially eliminated with phenol if the reaction is conducted below 60°C.^{46, 54}

Casting Resin. For each mole of phenol, 2.5 moles of formaldehyde as formalin solution is employed. The catalyst may be any alkali such as NaOH, KOH, or LiOH. Approximately 15 grams of 10% caustic per mole of phenol is typical with the reaction mixture being held at reflux temperature for 1¼–1½ hours. The resin is then cooled and neutralized to a pH of 5.5–6.5 with lactic, citric, or tartaric acid. Dehydration is carried out under a vacuum to a kettle temperature of 80–85°C./30 mm. Glycerine, 7–8% based on phenol, may be added just before completion of the dehydration. The glycerine will prevent clouding of the resin during cure and thus permit the formation of a clear casting.⁵⁶ The resins are usually cured by heating for 3–10 days at 70–85°C.

Oil-Soluble Heat-Reactive Resin. An oil-soluble heat-reactive resin may be conveniently prepared from a *p*-substituted phenol such as *p*-*tert*-amyl, *p*-*tert*-butyl, or *p*-phenylphenol as follows: 2.0–2.1 moles of formalin per mole of phenol is used. The reaction is catalyzed by 10–15 grams of 5 *N* caustic solution. The usual reaction period is 1½–2½ hours at reflux temperature. After cooling to room temperature the mixture is neutralized preferably with a dilute organic acid and washed thoroughly to remove salts. The oily layer is then dehydrated under a vacuum at a low temperature (60–80°C./30 mm.).

AMMONIA-CATALYZED RESOLES

Resoles prepared with ammonia as catalyst are more complex than those obtained with alkali metal hydroxides as catalysts. Ammonia, unlike the alkali metal hydroxides, causes almost immediate loss of water solubility in the resins.⁴² This has often led to the conclusion that phenol alcohols were not formed; however, both phenol mono- and dialcohols have been isolated from ammonia-catalyzed phenol-formaldehyde reaction mixtures.^{56,57} Largely through the efforts of Hultsch⁵⁸ and Zinke and coworkers⁵⁹⁻⁶⁷ it has been shown that, during the cure of novolac resins with hexamethylenetetramine, bis- and tris(hydroxybenzyl)amines are formed. More recently, Seto,⁶⁸ using chromatographic techniques, has found that compounds of this type as well as phenol alcohols are present in resoles prepared with ammonia as the catalyst. The bis- and tris(hydroxybenzyl)amines are not readily soluble in water. This could explain, at least partially, the rapid loss of water solubility of ammonia resoles. Small amounts of ammonia would be capable of converting a large part of the phenol in an ammonia resole into bis- and tris(hydroxybenzyl)amines. For example, 5% of concentrated ammonia based on the phenol would be capable of tying up as much as 25–31% of the phenol in a typical resin as a tris(hydroxybenzyl)amine.

Data obtained by the fractional precipitation of resins prepared with different catalysts show that the resins catalyzed with ammonia have a much higher melting point, and presumably a higher molecular weight, than resins prepared with caustic as catalyst. The amount of water-soluble resin in an ammonia resole is less than for a resin prepared with caustic as catalyst.⁴⁸ These data are consistent with the theory as to the structure of an ammonia resole as proposed above.

Ammonia resoles find considerable use in laminating varnishes. At least part of the cure of these resins is obtained by virtue of their methylol groups, although other means involving amine linkages, hexamethylenetetramine, etc., are possible. Further work is needed to provide detailed information on these questions. (See Chapter 5.)

The preparation of a typical ammonia resole is conducted as follows: To each mole of phenol add 1.1–1.15 moles of formaldehyde as formalin solution and 12–15 grams of concentrated ammonia. Reflux for 35–60 minutes, depending on the degree of condensation desired. Cool, and dehydrate under a vacuum, using an oil bath, until the temperature in the kettle reaches 75–80°C./30 mm. The resin is usually dissolved in alcohol to around 50% solids when used as a laminating varnish.

NOVOLAC RESINS

Novolac resins were named by Baekeland,^{12,69} who saw a superficial similarity in their properties to those of the lac resins. Most of the commercial novolac resins are made by the condensation of phenol with formaldehyde, although other aldehydes, such as furfural and acrolein, have had limited use.⁷⁰⁻⁷² Novolac resins are phenol-ended chain polymers in which the phenolic nuclei are joined by methylene bridges located *ortho* and *para* to the phenolic hydroxyl groups. The resins are almost invariably prepared with acidic catalysts, although non-catalyzed or even base-catalyzed reactions are occasionally employed.

The evidence for the linear polynuclear methylene bridge structure may be summarized as follows:

1. Separation of crystalline dihydroxydiphenylmethanes and other polynuclear methylene derivatives.
2. Preparation and analysis of derivatives.
3. Hydroxyl content, alkali solubility.
4. Non-curing properties and heat stability.
5. Decomposition of resins.
6. Infrared, ultraviolet, and X-ray data.
7. Dependence of molecular weight on mole ratio of reactants.

Probably the most convincing evidence for the methylene bridge structure has been the separation of products possessing such structures from the resins. The preparation and separation of crystalline dihydroxydiphenylmethanes have already been covered in Chapter 3. Small quantities of such products can be extracted from most novolac resins, regardless of the nature of the starting phenol, provided that the resin is not too highly condensed.

In order to be intermediates in resin formation the crystalline dihydroxydiphenylmethanes must be capable of reaction with additional aldehyde to give a resin. This point is well established. Indeed, dihydroxydiphenylmethanes can be used as the starting phenol for the preparation of a variety of useful resins, some with unique properties. Megson and Drummond⁷⁶ have shown that the quantity of dihydroxydiphenylmethanes, particularly certain isomers, which can be separated from a phenol-formaldehyde reaction mixture increases at first and then declines, showing that the compounds are early reaction products which are later consumed by resin formation.

Besides the dihydroxydiphenylalkanes, other, more complex poly-

nuclear methylene derivatives of phenols have been obtained in pure form. As the number of phenolic nuclei per molecule increases, the problems encountered in separating a single compound become very great. With phenol it is theoretically possible to form, by reaction only at the *ortho* and *para* positions, three two-ring, seven three-ring, twenty-one four-ring, and fifty-seven five-ring compounds.¹⁶ All the possible two-ring and the seven three-ring compounds have been separated in reasonable purity, but compounds with four or more rings have not been reported. Part of the problem of obtaining the longer-chain compounds is that a single isomer will not be formed in sufficient yield to permit isolation unless mass action or steric factors force the reaction in the direction of a single compound. A further complication arises because the polynuclear products are miscible with one another when melted and form solid solutions on cooling. Fractional crystallization of such mixtures is difficult because their solubilities are so similar and distillation is impossible except for the lower-molecular-weight compounds.

The difficulties arising from the formation of a great number of molecular species may, in part, be overcome by the use of *para*-substituted phenols. With such phenols there is only one two-ring, one three-ring, and one four-ring compound, etc. This obviously simplifies the problem of separating pure constituents. Koebner,⁷⁴⁻⁷⁶ who did much to establish the structure of novolac resins, was one of the first to take advantage of this. He was able to prepare the polynuclear methylene derivatives of *p*-cresol with from two to seven nuclei (see page 53). These materials resembled the commercial novolac resins in physical properties but were non-curing, owing to the difunctional nature of the starting phenol. This makes them resemble the oil-soluble novolac resins rather than the novolac resins used to prepare molding compounds.

Koebner's results, though very enlightening, left unanswered certain questions regarding the structure of the polynuclear products found in novolac resins capable of cure upon the addition of formaldehyde or hexamethylenetetramine. For many years the dihydroxydiphenylmethanes were the only polynuclear methylene derivatives of phenol that could be obtained in pure form. However, more recently a number of workers have obtained trinuclear derivatives of phenol, and now all seven of the possible isomers have been reported^{29, 77-80} (see Table I). Some difficulty was experienced by some of the workers in getting all the compounds to crystallize to sharp melting products. This is not too surprising since small amounts of one isomer cause a marked effect on the melting point of another isomer even when deal-

Table I

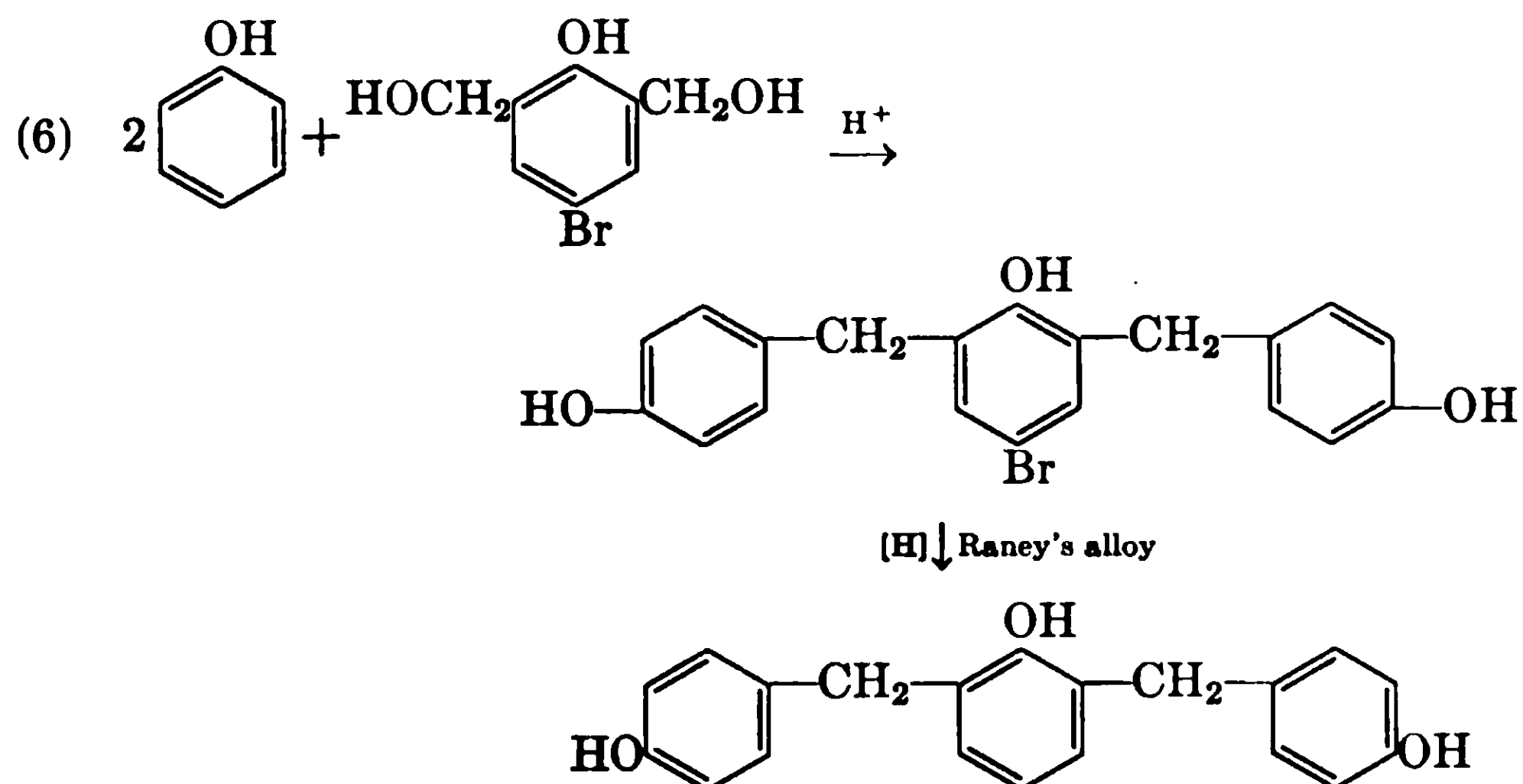
Trinuclear Phenol	M.P., °C.	Reference
2,4-Bis(2-hydroxybenzyl)phenol	118	29
	122-123	78
	122-123	80
2,4-Bis(4-hydroxybenzyl)phenol	145.5	29
	150	78
	149-150	80
2,6-Bis(2-hydroxybenzyl)phenol	158	29
	162	78
	161-162	80
2,6-Bis(4-hydroxybenzyl)phenol	171	29
	171	78
	171-171.6	80
2-(2-Hydroxybenzyl)-4-(4-hydroxybenzyl)phenol	56	29
2-(4-Hydroxybenzyl)-4-(2-hydroxybenzyl)phenol	133-134	29
2-(2-Hydroxybenzyl)-6-(4-hydroxybenzyl)phenol	133	29

ing with the two-ring systems.⁸¹ It has also been reported that the methylene derivatives of certain phenols are easily supercooled to a glass.⁸²

It has been suggested that the difference in the tendency for the isomeric products to separate into either the crystalline or resinous state may be traced to different rotational configurations in which the compounds may have separated.⁸⁰ It was suggested that one rotational configuration might be easily crystallized whereas another form might show a strong tendency to be resinous. Marked differences in the infrared and the ultraviolet absorption spectra of the 2,2'-dihydroxydiphenylmethanes as compared to the 2,4'- and 4,4'-dihydroxydiphenylmethanes also have been found. Ambelang and Binder⁸³ and Coggeshall⁸⁴ interpret the absorption data to mean that the phenols may exist in more than one form, e.g. a *cis* and a *trans* form. Ordinarily *cis* and *trans* isomers are considered to be fixed isomeric forms that may be found only when a carbon-carbon double bond is involved. In this instance the terms have been employed to designate structures where rotation around a single bond is hindered. Megson⁸⁵ claims that only with the 4,4'-dihydroxydiphenylmethanes is there free rotation around the methylene bridge (see page 144).

Bender⁸⁰ used two methods to prepare the three-ring compounds which he referred to as "triphenylols." Part of the compounds were obtained by the condensation of *o*- or *p*-hydroxybenzyl alcohol with one of three dihydroxydiphenylmethanes. *p*-Bromophenol dialcohol also was condensed with an excess of phenol to give a bromotriphenylol

which was reduced over Raney's alloy to the unsubstituted triphenylol, reaction 6. This is similar to the process used by Finn, Megson, and



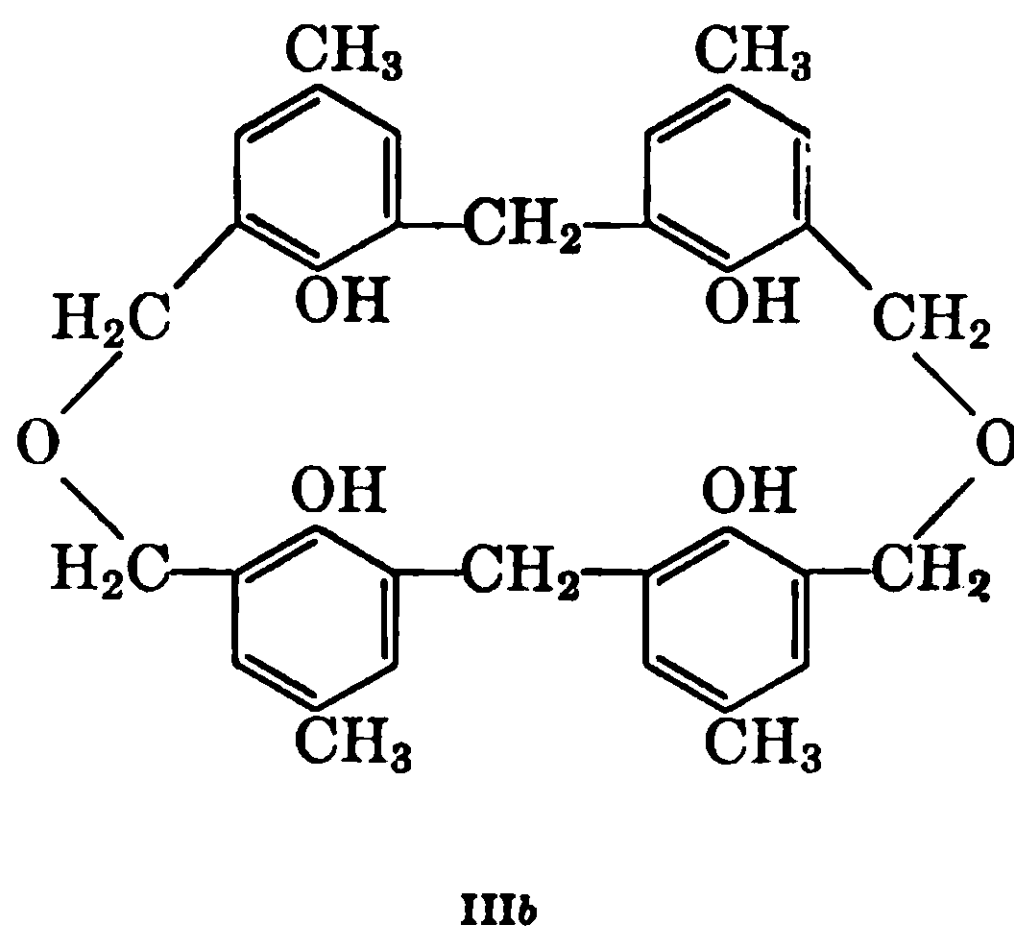
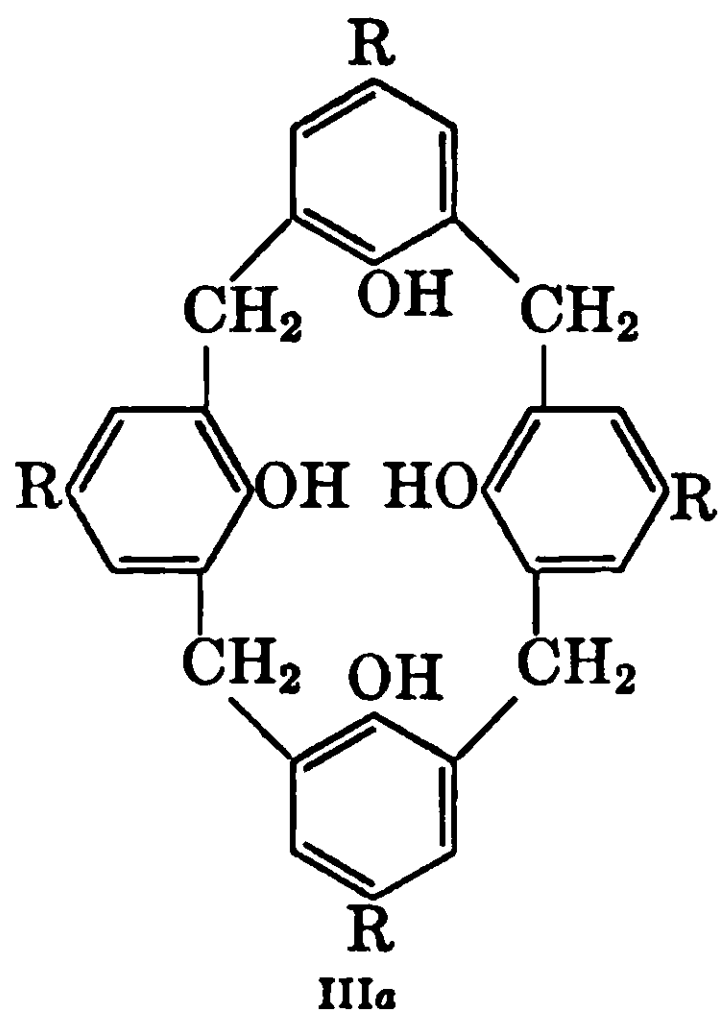
Whittaker⁸⁸ and by Finn, James, and Standen.²⁹ Bender eventually also obtained all the seven isomeric triphenylols from phenolic resins by a series of extractions.⁷⁹ This leaves little doubt that they are constituents of conventional novolac resins. The fact that they reacted normally with formaldehyde to give resins supports the point of view that they also may function as intermediates in the formation of higher-molecular-weight methylene derivatives. It is interesting to note that their rates of reaction with formaldehyde were not identical. When the triphenylols were mixed, resinous melts were formed that behaved like commercial novolac resins. However, the span in properties was greater than it is possible to obtain in commercial resins.

Davis, Hayes, and Hunter⁸⁷ have prepared some trinuclear and hexanuclear phenylols. The hexanuclear phenylol was of the non-curing type. As mentioned above, Finn, Megson, and Whittaker have prepared 2,6-bis(2-hydroxybenzyl)phenol. They reacted *p*-chlorophenol dialcohol with *p*-chlorophenol and then dechlorinated the product by the action of sodium in amyl alcohol. Finn and Lewis also prepared 2,6-bis(2-hydroxybenzyl)-3,5-xyleneol as well as several other trinuclear products.^{88, 89} A number of polynuclear phenols were prepared by Euler, Adler, deKispeczy and Fagerlund.⁹⁰ Pentanuclear products were obtained by the condensation of 2,4-dimethylphenol, *p*-cresol, and *p*-chlorophenol, respectively, with tetramethylolhydroquinone. These products were highly branched and for this reason do not resemble those found in novolac resins obtained by the condensation of phenols with aldehydes under acidic conditions. Trinuclear

products were obtained if dimethylolhydroquinone was substituted for the tertamethylol derivative. Several tetranuclear products have been obtained by the condensation of trimethylolphenol with various phenols.^{84, 91, 92} Polynuclear products also have been reported by Ziegler.^{93, 94}

In the face of the experimental evidence presented above, the conclusion seems inescapable that novolac resins are mixtures of chain polymers in which the phenolic nuclei are joined by methylene bridges and that the lower members may react further with aldehydes to form the higher-molecular-weight products. Data on the fractional precipitation of novolac resins indicate that the commercial resins may contain methylene derivatives with a wide disparity in molecular weight. Typical resins with an average molecular weight of 600 gave fractions with an average molecular weight ranging between a little over 200 to nearly 1300.⁹⁵ At an average molecular weight of around 1400, where the least soluble fraction had a molecular weight of around 5000, gelation was said to occur with a very small amount of extra formaldehyde.

Under certain conditions cyclic methylene derivatives, IIIa, or mixed cyclics, IIIb, which also have ether linkages, may be formed.⁹⁹⁻¹⁰⁰ These products are not common and need not be considered in a discussion of conventional novolac resins.



Numerous reports on the elemental analysis of novolac resins may be found in the literature.^{18, 95, 101-108} The analytical data agree well with the calculated values for products, assuming a polynuclear methylene structure, provided that the calculations are made for products of known molecular weight. That the phenolic hydroxyl

groups are intact has been shown by analysis for hydroxyl content,^{18, 85} the preparation of acetate, and benzoate esters, benzyl ethers, and phenyl isocyanate reaction products.^{103, 104} Analytical data on these derivatives also agree with calculated values assuming a methylene bridge structure for the novolac resin.

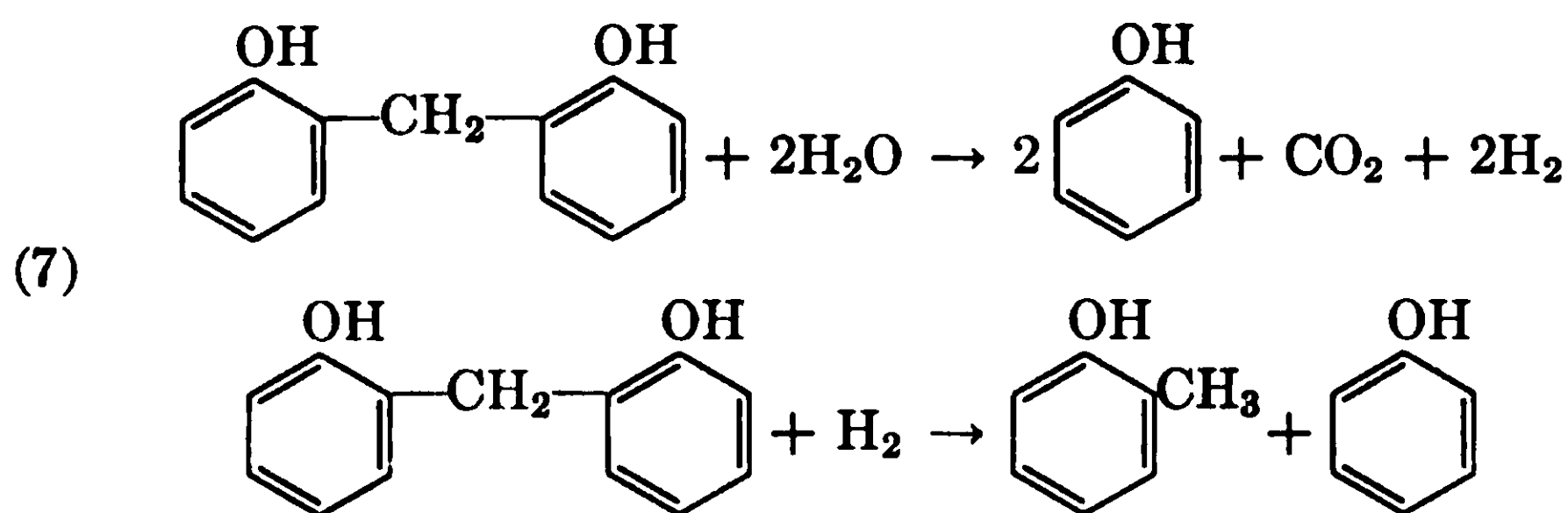
The presence of the phenolic hydroxyl group is also indicated by the alkali solubility of the resins. If the resin is of high molecular weight, its solubility in aqueous caustic may be very low. The resins form sodium salts, but the salts of the higher polymers are practically insoluble in caustic solution.⁷⁸ However, essentially all novolac resins are soluble in alcoholic potassium hydroxide solution.

When heated in an inert atmosphere below their point of decomposition, novolac resins remain permanently soluble and fusible. If heated in contact with air, a skin of reddish brown resin will form which is both insoluble and infusible. The formation of the insoluble and infusible skin is undoubtedly due to oxidative changes and not to the presence of methylol groups. It has been shown, for example, that dihydroxydiphenyls may be formed by the treatment of certain phenols with peroxides.¹⁰⁶ Similar reactions may be responsible for the cross linking of novolac resins on exposure to air, although such a coupling reaction has not been proved conclusively for phenolic resins. Heating in the presence of air may also bring about degradative changes which will decrease the molecular weight of the higher-viscosity novolac resins. Such reactions have been reported to occur even in the solid state and at temperatures as low as 70°C.¹⁰⁸ Bender¹⁰⁷ thinks that some linkages are much less stable than other linkages, particularly in the higher-viscosity novolac resins.

Methylol groups were not detected in a commercial novolac resin by Martin.¹⁰⁸ Vanscheidt¹⁸ and Müller and Müller⁸⁸⁽⁹⁾ have also reported similar results using entirely different methods of analysis. Later by means of chromatographic techniques which are much more sensitive than the methods of the above workers, phenol alcohols were found in small amounts of novolac resins, especially during the early stages of their preparation.²⁹ However, these findings do not alter the over-all picture of a novolac resin, since the phenol alcohols were minor constituents, present in insufficient quantity to make the resins self-curing.

Several workers have studied the decomposition of phenolic resins. Herzog¹⁰⁹ found that phenol could be recovered by digesting various phenolic resins with caustic. Allen, Meharg, and Schmidt¹¹⁰ also used caustic but carried out the reaction in an autoclave at 300°C. They found that the decomposition products always contained more

of the methyl-substituted phenols than the phenol from which it was made. The methyl substituents appeared to be derived from the combined formaldehyde since the higher phenols were obtained in greater quantity from the more advanced resins as well as from resins prepared with a higher ratio of formaldehyde to phenol. As hydrogen was evolved, the net effect was given as shown below, reaction 7.



Waterman and Veldman¹¹¹ studied the decomposition of resins under hydrogen pressure, using molybdenum as catalyst. They argued that at the point of decomposition hydrogen atoms are needed, and, if they are not present, complicated side reactions could occur. The products from the reductive decomposition of novolac resins were phenol, benzene, cresols, and toluene.

Megson^{26, 112} studied the purely thermal decomposition of novolac resins by heating purified resins in a flask up to 450°C. after removing volatile products under a vacuum. Megson set up a typical resin molecule and postulated cleavage at various points along the chain to explain the products obtained. Starting with a novolac resin prepared from phenol, Megson found only *o*- and *p*-cresol and phenol in the alkali-soluble portion of the distillate. In the neutral portion of the distillate, xanthene and methyl derivatives of xanthene were present, presumably formed by dehydration of 2,2'-dihydroxydiphenylmethanes. All the products found by Megson, who also worked with resins from *o*-, *m*-, and *p*-cresol, support the assumption that novolac resins are chain molecules in which the phenolic nuclei are joined by methylene bridges.

Bender¹⁰⁷ explains the recovery of phenol from heating a novolac resin by making use of the principle of mass displacement. He reports that a novolac resin upon being heated with a large excess of any high-boiling phenol stable at 250°C. will cause lower-boiling phenols to be displaced and recovered from such reaction mixtures. In line with Bender's proposal, Carpenter and Hunter⁹¹ found that, in the presence of a trace of acid, the tetraphenol obtained by reacting

trimethylolphenol with *p*-cresol could be converted to a dihydroxydiphenylmethane upon refluxing with an excess of *p*-cresol. (Also see Chapter 9 for rottlerone change.)

Absorption data have been used to help elucidate the structure of both cured and uncured phenolic resins. deBoer, Houwink, and Custers¹¹⁸ found that the spectra of cured and uncured resins gave essentially identical absorption curves between 2300 and 3750 Å. The absorption spectra of the cured resins resemble the spectra of the alkyl phenols but do not resemble the spectra of the phenolic ethers, indicating that the methylene bridges are attached to the benzene rings and not to the phenolic hydroxyl groups. Thompson and co-workers¹¹⁴ have made a careful study of the infrared spectra of phenolic resins as well as of the simpler intermediates; Hunter, Morton, and Carpenter¹¹⁵ and Mayer-Pitsch and Troger¹¹⁶ have made similar studies of the ultraviolet absorption spectra of such materials. A difference in the amount of hydrogen bonding between the phenolic hydroxyl groups of *ortho*, *ortho* and *para*, *para* dihydroxydiphenylmethanes has been found as a result of absorption studies.^{88, 84, 114, 117} This difference in hydrogen bonding carries over to the novolac resins. The amount of hydrogen bonding and in turn the amount of *ortho*, *ortho* methylene bridges in a resin have an effect on the reactivity of the resins toward curing agents. X-ray studies of the crystalline dihydroxydiphenylmethanes, as well as of the higher homologs, have been made by several workers.^{88, 118, 119}

A final argument for the presence in novolac resins of an alternating phenol and methylene bridge is the dependence of molecular weight on the ratio of reactants. According to the theories of functionality, the maximum chain length should be attained when the phenol and formaldehyde are reacted in equal molar quantities, provided that the phenol is of the difunctional type. Where the phenol is trifunctional, the molecular weight should increase steadily with the ratio of formaldehyde to phenol until gelation sets in. In actual practice it has been found that a resin showing very little branching or cross linking is formed provided that the phenol is used in slight excess.⁴⁸ Pollack and Riesenfeld¹²⁰ report that lumps of gel begin to appear when the ratio of formaldehyde to phenol is increased from 6.04 to 6.075 moles of formaldehyde to 7 moles of phenol. Koebner¹²¹ also performed a series of experiments with *p*-cresol which demonstrates very admirably the effect we are discussing. He started by reacting 10 moles of *p*-cresol with 1 of formaldehyde under carefully controlled conditions. In successive experiments he increased the amount of formaldehyde 1 mole at a time until 7 moles of formaldehyde were being used for

each 10 moles of *p*-cresol. The average molecular weight of the products, after removal of unreacted *p*-cresol, increased in a regular fashion from 229 to 638. With phenol, between a ratio of 1.25 to 10 moles of phenol per mole of formaldehyde, Vanscheidt¹⁸ found that the molecular weight of the resin agreed approximately with that calculated from the yield of resin:

$$M = 94A/(A - 106)$$

where M is the average molecular weight of the resin and A is the yield of resin per mole of reacted aldehyde. These data indicate that in the formation of a novolac resin n moles of formaldehyde react with $n + 1$ moles of phenol.

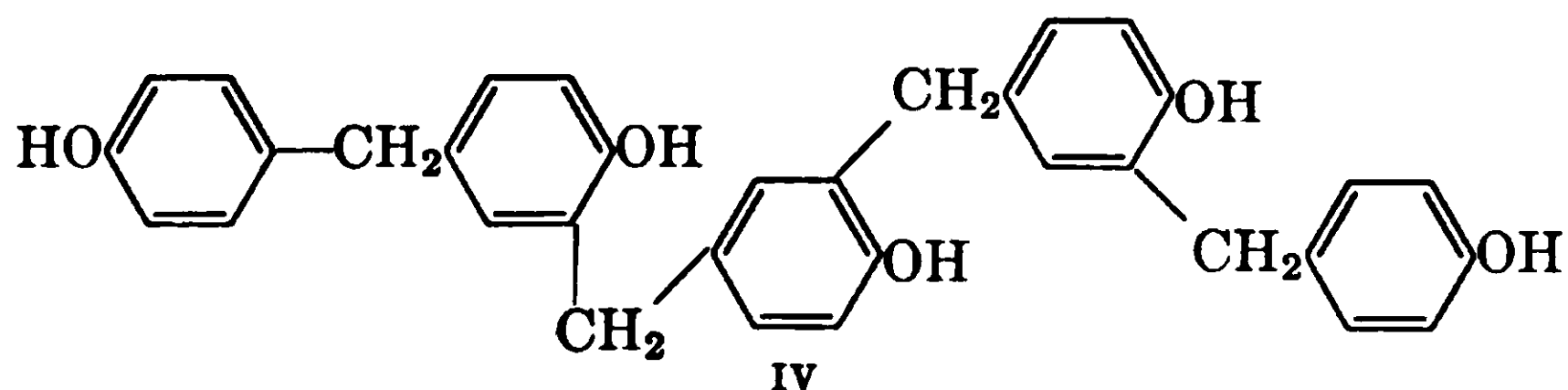
Structural Details

One further point regarding the structure of novolac resins warrants discussion, namely, the shape of the resin chain. Are the chains of a novolac resin branched or linear, and, if branched, to what extent? Apparently, the method of preparation plays a dominant role in this respect. The conventional resins, prepared with acidic catalysts, appear to be essentially linear. This appears to be true even when the resin is prepared from a trifunctional phenol where branching is at least theoretically quite possible. Vanscheidt, in particular, has made detailed studies of the viscosities of phenolic resins, including the novolac resins, in various solvents.⁵² His data strongly support an essentially linear structure. The viscosity of novolac resins prepared from *para*-substituted phenols, which must be essentially linear, is very similar to that of the novolac resins prepared with trifunctional phenols with acidic catalysts. On the other hand, novolac resins prepared by the condensation of resoles with excess phenol are highly branched. These novolac resins show pronounced differences in viscosity when compared to novolac resins prepared in a more conventional manner by direct reaction of phenols with formaldehyde under acidic conditions. A model of a highly branched novolac resin was prepared by Vanscheidt by condensing tetramethyloldiphenylolmethane with an excess of phenol. This product, which was called an "isonovolac," showed approximately twice the viscosity of the conventional novolac resins.

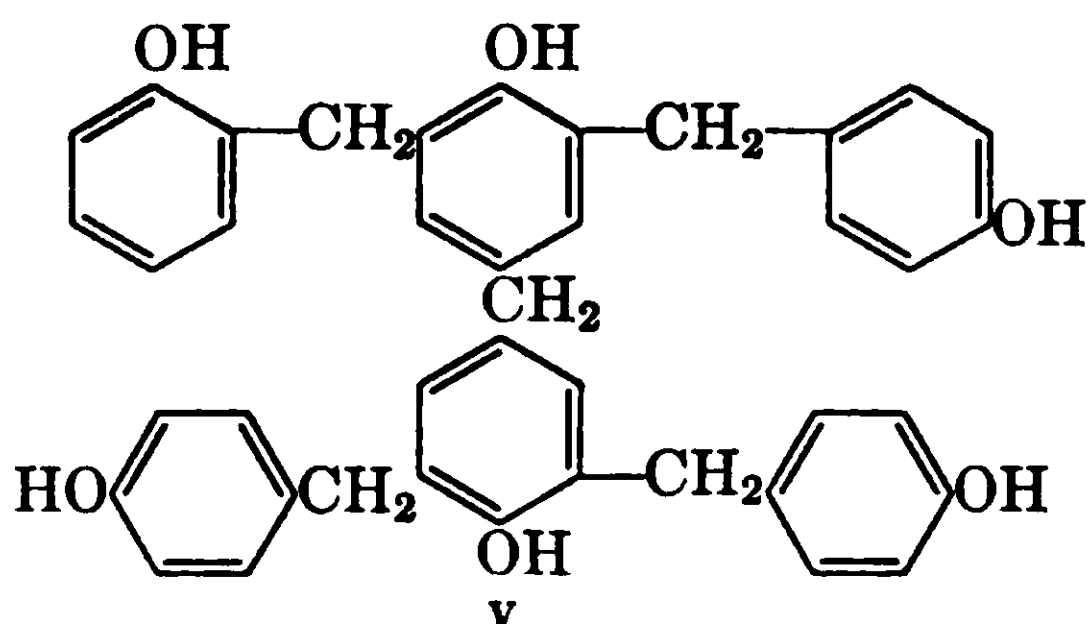
A tremendous amount of time and effort has gone into studies on the numerous variables that affect the properties of commercial novolac resins. Particular emphasis has been given to correlating the method of manufacture with resin performance when incorporated into a mold-

ing compound. Some of the more important properties of a resin affected by manufacturing conditions are melting or flow point, viscosity, rate of cure with hexamethylenetetramine, amount of branching, location of methylene bridges, and rigidity of cured resin. Factors which affect the above properties, in addition to the starting phenol, are catalyst and catalyst concentration, reaction time and temperature, mole ratio of reactants, method of dehydration, heating schedule, etc. Many of these variables have been adequately covered elsewhere and will not be treated in detail here. However, discoveries on the effect of the catalyst on resin structure and performance merit our attention.

Besides affecting the amount of branching in a novolac resin, the catalyst may also affect the location of the methylene bridge between the phenol rings. It is now generally accepted that acidic catalyst tends to favor the formation of *p,p'*-linkages, although *o,p'* or even *o,o'*-linkages may also be formed. It is quite obvious that, as the chain length exceeds two phenol rings, the third mole of phenol cannot be added to a *p,p'*-dihydroxydiphenylmethane through a *p,p'*-linkage since all the *para* positions have already been used. The result will be that, after the first *p,p'*-linkage is formed, the next methylene bridge will be between an *ortho* position of the dihydroxydiphenylmethane and presumably at the *para* position of the phenol molecule being added to the chain. A highly idealized novolac resin molecule based on these assumptions is shown below (IV).



Strong alkalies show a strong tendency to catalyze the formation of phenol polyalcohols which, if reacted with excess phenol, would give a highly branched novolac resin (V). Resins of this type have not found



wide acceptance.

Certain metal oxides may also be used as catalysts for the preparation of novolac resins. Because of their rapid cure and other special properties, these resins are undergoing active commercial exploitation. The development of the fast-curing resins was the result of detailed basic studies by Bender and his coworkers at Bakelite.^{117, 122-125} The group started their studies by preparing all six possible isomeric dihydroxydiphenylmethanes (Table II). Procedures were used that left

Table II

Diphenylolmethane	Melting Point, °C
2,2'-	118.5-119.5
2,3'-	95.5-96
2,4'-	119-120
3,4'-	116-116.5
3,3'-	102-103
4,4'-	162-163

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no doubt as to the location of the methylene bridge in each compound. When these dihydroxydiphenylmethanes were heated with hexamethylenetetramine or treated with formaldehyde, marked differences in reactivity were observed. The 2,2'-isomer, in particular, showed an unusually high rate of cure when heated with hexamethylenetetramine (see Table III). Since formaldehyde reacts with phenol under normal

Table III

Diphenylol- methane	Gel Time, seconds	
	Diphenol	Resin
2,4'-	240	61
4,4'-	175	46
2,3'-	140	
3,4'-	130	
3,3'-	120	
2,2'-	60	17

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conditions only at the *ortho* and *para* position, only three of the six isomers, namely, 2,2'-, 2,4'-, and 4,4'-dihydroxydiphenylmethane, are theoretically possible by the direct reaction of phenol with formaldehyde. Of these three isomers, only the last two had previously been found in phenol-formaldehyde reaction mixtures. The 2,2'-isomer

had been reported previously, but had been prepared by indirect means.¹²⁶

By study of reaction conditions, Bender and his coworkers discovered that the desired highly reactive 2,2'-isomer could be obtained in appreciable yields if an excess of phenol were reacted with formaldehyde at elevated temperatures in the presence of certain metal oxide catalysts, e.g., zinc, magnesium, or aluminum oxide. By suitable modification of reaction conditions, but with these same catalysts, novolac resins possessing in excess of 50% of the 2,2'-structure were also obtained. That the rapid-curing properties of the 2,2'-dihydroxydiphenylmethane were carried over to the resins high in the 2,2'-structure may be seen by inspection of the data in Table III. Bender states that "varying percentages of the 2,2'-content are possible by careful control of reaction conditions which include catalyst, temperature, pH, ratio of reactants, and reaction time."¹¹⁷ Finn and Musty¹²⁷ later made a detailed study of the effect of pH. Analytical methods based on infrared absorption and bromination data were developed by Bender to determine the amount of 2,2'-linkages in a resin. The control of resin cure speed by varying the amount of 2,2'-structure in a Two-Stage resin is probably the most significant development during the recent history of phenolic resins. Not only is it possible to produce resins by this means with more rapid cure rates, but also moldings prepared from molding compounds based on such resins have the advantage of increased "hot rigidity" which tends to cut down on warpage when the moldings are ejected from a hot mold.

Manufacturing Procedures

Some more or less general comments on manufacturing procedure are in order. As mentioned previously on several occasions, acidic catalysts are most frequently employed in preparing novolac resins. Sulfuric acid is often favored because of price, lack of volatility, and ease in handling. Oxalic acid is one of the best catalysts for the production of light-colored resins, although phosphoric acid also gives better than average color. Acids soluble in the resin layer, such as *p*-toluenesulfonic acid, give better formaldehyde and phenol utilization than water-soluble catalysts. Surface-active agents promote the reaction of the higher alkyl phenols that have low solubility in formalin.¹²⁸ High concentrations of acids are to be avoided so that the reaction does not become so vigorous as to be difficult to control. Too much acid may also cause excessive bodying of the resin.

Koebner¹²¹ has described the preparation of a novolac resin by re-

action of 10 moles of phenol with 5 moles of formalin in the presence of ammonia. In order to obtain a novolac resin from this combination of reactants, certain requirements as to reaction procedure have to be met. If a vacuum is applied immediately after the condensation reaction and the water and excess phenol is removed at a low temperature, a curing resin results. However, if the water is boiled off at atmospheric pressure and the resin is slowly raised to 160°C. before the excess phenol is removed under a vacuum, a novolac resin results. Apparently, the phenol alcohols or amine analogs, formed by the basic catalyst, condense at the high temperature used in the latter procedure to give methylene derivatives. At the low temperature maintained during the vacuum dehydration the active groups remain intact. In the absence of excess phenol, which is removed under vacuum, these groups confer curing properties to the resin.

A type of novolac resin also can be prepared by using a strong alkaline catalyst provided that a large excess of phenol is used coupled with a long reaction period at high temperature. A similar product is obtained by the addition of a resole to an excess of phenol under acidic conditions. This reaction is analogous to the synthesis of dihydroxydiphenylmethanes by the condensation of phenol alcohols with phenols. The patent literature describes a novolac resin prepared from phenol and formaldehyde where the reaction was started under alkaline and finished under acidic conditions.¹²⁹ The ratio of phenol to formaldehyde was high, and the dehydration of the resin was conducted at atmospheric pressure.

Paraform, trioxane, and even hexamethylenetetramine may be used in the place of aqueous formaldehyde for the preparation of novolac resins.¹³⁰⁻¹³² Particularly with paraform, care must be taken to avoid a runaway reaction. However, paraform has the advantage of cutting down on the amount of water that must be removed from the resin at the end of the reaction. It may be used both for the preparation and as a curing agent for resorcinol resins.^{133, 134} Alcohol solutions of formaldehyde are available commercially and have been used in resin manufacture. The alcohol solutions are used more frequently for the preparation of One-Stage than of the Two-Stage type. The alcohol serves as the solvent for the finished resin when reaction is complete and is useful for laminating resins where alcohols are often employed as solvents.

Novolac resins have occasionally been prepared without the benefit of an added catalyst.¹³⁵ Because of the low reactivity of phenols with formaldehyde in the absence of catalysts high temperatures are required. The early resins of this type were prepared in autoclaves.

More recently tube reactors have been used. This permits better control of reactions at the high temperatures required when a catalyst is not employed.

For the preparation of a typical novolac resin, 1 mole of phenol to each 0.83 mole of formalin is charged to a reaction vessel. Approximately 0.2–0.3% of concentrated sulfuric acid, based on the phenol, is added after dilution to about 1 *N* with water. An exothermic reaction takes place on addition of the catalyst or upon warming slightly. When the exothermic reaction has spent itself, the reaction mixture is refluxed for 1–2 hours. At this point the resin is usually neutralized by the addition of a slight excess of lime made into a slurry with water. The resin is dehydrated under a vacuum and discharged from the kettle onto a cold floor. The cooled resin is broken into lumps and ground preparatory to compounding with fillers, hexamethylenetetramine, pigments, etc., to make a Two-Stage molding resin. The flow point of the resin will depend on the ratio of reactants as well as on the degree of dehydration. If an oil-soluble novolac resin from a *p*-substituted phenol is desired, it may be necessary to use a surface-active agent to promote contact between the phenol and the formalin and to extend the reaction time.

REFERENCES FOR CHAPTER 4

- ¹ E. Imoto, *J. Soc. Chem. Ind., Japan*, **45**, 1053 (1942); **46**, 520 (1943); **46**, 800 (1943); **47**, 178–189 (1944); **47**, 359 (1944); **47**, 657–660 (1944); **47**, 824 (1944); **49**, 61 (1948).
- ² A. P. Dunlop and F. N. Dunlop, *Colloid Chemistry*, Vol. VI, Reinhold Publishing Corp., New York, 1946, p. 1048.
- ³ A. Porai-Koschutz, N. Kudryanzeff, and B. Maschkileisen, *Kunststoffe*, **23**, 97–100 (1933).
- ⁴ L. V. Redman and A. V. H. Mory, *Ind. Eng. Chem.*, **23**, 595–597 (1931).
- ⁵ L. H. Baekeland, *J. Ind. Eng. Chem.*, **1**, 149–161 (1909).
- ⁶ T. S. Carswell, *Phenoplasts*, Interscience Publishers, New York, 1947.
- ⁷ C. Ellis, *The Chemistry of Synthetic Resins*, Reinhold Publishing Corp., New York, 1935.
- ⁸ H. Lebach, *J. Soc. Chem. Ind.*, **28**, 803 (1909).
- ⁹ H. Lebach, *Z. angew. Chem.*, **22**, 1598 (1909).
- ¹⁰ H. Lebach, *J. Soc. Chem. Ind.*, **32**, 559–564 (1913).
- ¹¹ L. H. Baekeland, *J. Ind. Eng. Chem.*, **1**, 545–549 (1909).
- ¹² L. H. Baekeland, *J. Ind. Eng. Chem.*, **4**, 737–743 (1912).
- ¹³ A. Zinke, *J. Applied Chem.*, **1**, Pt. 6, 257–266 (1951).
- ¹⁴ A. Zinke, F. Hanus, and E. Ziegler, *J. prakt. Chem.*, (2), **152**, 126–144 (1939).
- ¹⁵ A. Zinke and E. Ziegler, *Wiener Chem. Ztg.*, **47**, 151–184 (1944).
- ¹⁶ N. J. L. Megson, *J. Soc. Chem. Ind.*, **52**, 420–424T (1933).
- ¹⁷ E. Ziegler and G. Zigeuner, *Kunststoffe*, **39**, 191–192 (1949).

- ¹⁸ A. Vanscheidt, *Org. Chem. Ind. U.S.S.R.*, **3**, 385-393 (1937).
¹⁹ K. Hultsch, *Chemie der Phenolharze*, Springer Verlag, Berlin, 1950.
²⁰ M. M. Sprung and M. T. Gladstone, *J. Am. Chem. Soc.*, **71**, 2907-2913 (1949).
²⁰⁰ J. Reese, *Kunststoffe*, **45**, No. 4, 137-145 (1955).
²¹ A. Zinke and E. Ziegler, *Ber.*, **74**, 541-545 (1941).
²² E. Adler, S. Tingstam, and A. O. Caspersson, *Arkiv Kemi Mineral. Geol.*, **B15**, No. 10, 1-8 (1942).
²³ H. S. Lilley, *J. Soc. Chem. Ind.*, **67**, 196-199 (1948).
²⁴ F. Raschig, *Z. angew. Chem.*, **25**, 1947 (1912).
²⁵ F. Raschig, *Kunststoffe*, **27**, 51-55 (1937).
²⁶ N. J. L. Megson, *Trans. Faraday Soc.*, **32**, 336-345 (1936).
²⁷ J. Scheiber and R. Barthel, *J. prakt. Chem.*, **147**, 99-109 (1936).
²⁸ A. T. Carpenter and R. F. Hunter, *J. Applied Chem.*, **1**, Pt. 5, 217-226 (1951).
²⁹ S. R. Finn, J. W. James, and C. J. S. Standen, *Chemistry & Industry*, Feb. 13, 1954, p. 188.
³⁰ K. Auwers, *Ber.*, **50**, 2524 (1907).
³¹ K. Fries and K. Kann, *Ann.*, **355**, 335-356 (1907).
³² T. Zincke and C. von Hohorst, *Ann.*, **353**, 357-379 (1907).
³³ R. Barthel, *Plastica (Holland)* **2**, 247-251 (1949).
³⁴ J. H. Freeman and C. W. Lewis, *J. Am. Chem. Soc.*, **76**, 2080-2087 (1954).
³⁵ G. Zigeuner and E. Ziegler, *Monatsh.*, **79**, 89 (1948).
³⁶ E. Ziegler and G. Zigeuner, *Monatsh.*, **79**, 358-362 (1948); **79**, 42-54 (1948).
³⁷ E. Ziegler, G. Zigeuner, and A. Kainzner, *Monatsh.*, **80**, 295-302 (1949).
³⁸ P. W. Neber and P. Kubitzky, Dissertation by P. Kubitzky, Tübingen, 1937. E. Marder and I. W. Ruderman, *J. Am. Chem. Soc.*, **73**, 5475-5476 (1951).
³⁹ J. H. Freeman, private communication.
⁴⁰ W. Huckel, *Theoretische Grundlagen der organische Chemie*, Becker and Erler, Leipzig, 1943, p. 281.
⁴¹ F. S. Granger, *Ind. Eng. Chem.*, **29**, 860, 1125 (1937).
⁴² K. B. Goldblum, Preprint *Bull. Div. Paint, Varnish and Plastics Chem.*, American Chemical Society Meeting, September, 1950, pp. 60-67.
⁴³ L. Bettelheim and K. Nihlberg, *Svensk Kem. Tid.*, **59**, 31-57 (1947); *Brit. Plastics*, **20**, 50, 108 (1948).
⁴⁴ A. Lewin and P. Robitschek, *Brit. Plastics*, **1945**, 316-322, 385-391.
⁴⁵ J. J. Smith, F. M. Rugg, and H. M. Bowman, *Anal. Chem.*, **24**, 497 (1952).
⁴⁶ A. A. Vanscheidt and A. A. Vasiliev, *J. Applied Chem. U.S.S.R.*, **19**, 7 (1946).
⁴⁷ R. W. Bentz and H. A. Neville, *J. Polymer Sci.*, **4**, 673-688 (1949).
⁴⁸ T. G. Harris and H. A. Neville, *J. Polymer Sci.*, **10**, 19-28 (1953).
⁴⁹ F. S. Granger, *Ind. Eng. Chem.*, **24**, 442-447 (1932); **29**, 1305-1308 (1937).
⁵⁰ K. Oshima and E. Imoto, *Chem. High Polymers (Japan)*, **3**, 65-67 (1946).
⁵¹ A. Vanscheidt, A. Itenberg, and G. Shtraikham, *Narodnyi Komissariat Tyazheloi Prom. S.S.S.R., Shornik*, **2**, 145-159 (1937).
⁵² A. A. Vanscheidt, *Soedineniyam, Akad. Nauk S.S.S.R., Otdel. Khim. Nauki Otdel. Fiz.-Mat. Nauk*, **1**, 20-21 (1943).
⁵³ H. F. Müller and I. Müller, *Kunststoffe*, (a) **42**, 57-63 (1952); (b) **41**, 186-188 (1951); (c) **38**, 221 (1948); (d) **38**, 25-44 (1948); (e) **37**, 75 (1947).
⁵⁴ R. W. Martin, *J. Am. Chem. Soc.*, **73**, 3952-3954 (1951); U. S. pat. 2,579,329 (1951).
⁵⁵ O. Pantke, U. S. pats. 1,909,786; 1,909,787; 1,909,788; 1,909,789 (1933).
⁵⁶ R. W. Martin, *J. Am. Chem. Soc.*, **74**, 3024-3025 (1952).

- ⁶⁷ I. W. Ruderman, *J. Soc. Chem. Ind.*, **64** No. 7, 204 (1945).
- ⁶⁸ K. Hultsch, *Chem. Ber.*, **82**, 16-25 (1949).
- ⁶⁹ A. Zinke and St. Pucher, *Monatsh.*, **79**, 26-41 (1948).
- ⁶⁰ A. Zinke, G. Zigeuner, G. Weisz, and Leupold-Löwenthal, *Monatsh.*, **81**, 1098-1107 (1950).
- ⁶¹ A. Zinke, G. Zigeuner, and G. Weisz, *Monatsh.*, **80**, 148-150 (1949).
- ⁶² A. Zinke, G. Zigeuner, G. Weisz, and E. Wiesenberger, *Monatsh.*, **80**, 160-169 (1949).
- ⁶³ A. Zinke, G. Zigeuner, G. Weisz, and W. Schaden, *Monatsh.*, **81**, 999-1006 (1950).
- ⁶⁴ G. Zigeuner, W. Schaden, *Monatsh.*, **81**, 1017-1023 (1950).
- ⁶⁵ G. Zigeuner, W. Schaden, and O. Gabriel, *Monatsh.*, **81**, 1108-1112 (1950).
- ⁶⁶ A. Zinke, F. Hanus, and H. Pichelmayer, *Monatsh.*, **78**, 311-316 (1948).
- ⁶⁷ A. Zinke, G. Zigeuner, and G. Weisz, *Monatsh.*, **80**, 160-169 (1949).
- ⁶⁸ S. Seto, in press.
- ⁶⁹ L. H. Baekeland, *J. Ind. Eng. Chem.*, **5**, 506 (1913).
- ⁷⁰ G. R. Owens, U. S. pat. 2,348,408.
- ⁷¹ J. P. Trickey, C. S. Miner, and H. J. Brownlee, *Ind. Eng. Chem.*, **15**, 65 (1923).
- ⁷² L. H. Brown, *Ind. Eng. Chem.*, **44**, 2673 (1952).
- ⁷³ N. J. L. Megson and A. A. Drummond, *J. Soc. Chem. Ind.*, **49**, 251-257T (1930).
- ⁷⁴ M. Koebner, *Brit. Plastics*, **11**, 7-9, 43 (1939).
- ⁷⁵ M. Koebner, *Chem. Ztg.*, **54**, 619 (1930).
- ⁷⁶ M. Koebner, *Z. angew. Chem.*, **46**, 251-256 (1933).
- ⁷⁷ Union Carbide & Carbon Corp., Brit. pat. 707,598 (1954).
- ⁷⁸ J. Reese, *Angew. Chem.*, **66**, No. 6, 170 (1954).
- ⁷⁹ H. L. Bender, A. G. Farnham, J. W. Guyer, F. N. Apel, and T. B. Gibb, Jr., Preprint *Bull., Div. Paint, Varnish and Plastics Chem.*, American Chemical Society Meeting, September, 1950, pp. 73-77.
- ⁸⁰ H. L. Bender, et al., *Ind. Eng. Chem.*, **44**, 1619-1623 (1952).
- ⁸¹ R. S. Finn, G. J. Lewis, and N. J. L. Megson, *J. Soc. Chem. Ind.*, **69**, S51-S53 (1950).
- ⁸² N. J. L. Megson, *J. Soc. Chem. Ind.*, **67**, 155-160 (1948).
- ⁸³ J. C. Ambelang and J. L. Binder, *J. Am. Chem. Soc.*, **75**, 947 (1953).
- ⁸⁴ N. D. Coggeshall, *J. Am. Chem. Soc.*, **72**, 2836 (1950).
- ⁸⁵ N. J. L. Megson, paper presented at International Congress on Plastics, Paris, January, 1949.
- ⁸⁶ S. R. Finn, N. J. L. Megson, and E. J. W. Whittaker, *Chemistry & Industry*, S849-S853 (1950).
- ⁸⁷ A. C. Davis, B. T. Hayes, and R. F. Hunter, *J. Applied Chem.*, **8**, Pt. 7, 312 (1953).
- ⁸⁸ S. R. Finn and G. J. Lewis, *J. Applied Chem.*, **1**, Pt. 11, 524-526 (1951).
- ⁸⁹ S. R. Finn and G. J. Lewis, *J. Soc. Chem. Ind.*, **69**, 132 (1950).
- ⁹⁰ H. von Euler, E. Adler, S. deKispeczy, and A. Fagerlund, *Arkiv Kemi Mineral. Geol.*, **A14**, No. 10, 1-20 (1940).
- ⁹¹ A. T. Carpenter and R. F. Hunter, *J. Chem. Soc.*, 1954, 2731.
- ⁹² J. H. Freeman, *Anal. Chem.*, **24**, 955 (1952).
- ⁹³ E. Ziegler, *Monatsh.*, **79**, 142-147 (1948).
- ⁹⁴ E. Ziegler, I. Hontschik, and L. Milowis, *Monatsh.*, **78**, 334-342 (1948).

- ⁹⁵ A. Vanscheidt, A. Itenberg, and T. Andreeva, *Ber.*, 69, 1900 (1936).
- ⁹⁶ J. B. Niederl and J. S. McCoy, *J. Am. Chem. Soc.*, 65, 629 (1943).
- ⁹⁷ H. von Euler, E. Adler, and B. Bergstrom, *Arkiv Kemi Mineral. Geol.*, B14, No. 30, 1-6 (1941).
- ⁹⁸ A. Zinke, E. Ziegler, et al., *Ber.*, 77, 264-272 (1944).
- ⁹⁹ A. Zinke, G. Zigeuner, K. Hössinger, and G. Hoffman, *Monatsh.*, 79, 438 (1948).
- ¹⁰⁰ J. B. Niederl and H. J. Vogel, *J. Am. Chem. Soc.*, 62, 2512 (1940).
- ¹⁰¹ H. P. Kaufmann, *Fette u. Seifen*, 44, 150 (1937).
- ¹⁰² W. Norman and E. Schildknecht, *Fettchem. Umschau*, 40, 194 (1933).
- ¹⁰³ A. Vanscheidt, A. Itenberg, P. Erluikova, and G. Simonov, *Plasticheskie Massui*, No. 3, 17-25 (1934).
- ¹⁰⁴ W. Kern, G. Dall-Asta, and H. Kammerer, *Makromolekulare Chem.*, 8, 252-267 (1952).
- ¹⁰⁵ F. H. Seubold, F. F. Rust, and W. E. Vaughn, U. S. pat. 2,490,282.
- ¹⁰⁶ R. W. Hall, *Chemistry & Industry*, 28, 693 (1952).
- ¹⁰⁷ H. L. Bender, private communication.
- ¹⁰⁸ R. W. Martin, *Anal. Chem.*, 23, 883-884 (1951); data on methylol content of novolac resins is unpublished work.
- ¹⁰⁹ W. Herzog, *Z. angew. Chem.*, 34, 97 (1921).
- ¹¹⁰ I. Allen, V. E. Meharg, and J. H. Schmidt, *Ind. Eng. Chem.*, 26, 663-669 (1934).
- ¹¹¹ H. I. Waterman and A. R. Veldman, *Brit. Plastics*, 8, 125-128, 182-184 (1936).
- ¹¹² N. J. L. Megson, *J. Soc. Chem. Ind.*, 58, 131-139 (1939).
- ¹¹³ J. H. deBoer, R. Houwink, and J. F. H. Custers, *Rec. trav. chim.*, 52, 709-718 (1933).
- ¹¹⁴ R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1947, 293, 1260.
- ¹¹⁵ R. F. Hunter, R. A. Morton, and A. T. Carpenter, *J. Chem. Soc.*, 1950, 441.
- ¹¹⁶ E. Mayer-Pitsch and H. Troger, *Z. Elektrochem.*, 47, 60-65 (1941).
- ¹¹⁷ H. L. Bender, *Modern Plastics*, February, 1953, 136-138, 220-222; March, 1954, 115-118, 200.
- ¹¹⁸ R. F. Hunter and V. Vand, *J. Applied Chem.*, 1, Pt. 7, 298-300 (1951).
- ¹¹⁹ N. J. L. Megson and W. A. Wood, *Nature*, 140, 642-643 (1937).
- ¹²⁰ F. Pollack and F. Riesenfeld, *Z. angew. Chem.*, 43, 1129-1132 (1930).
- ¹²¹ M. Koebner, *Brit. Plastics*, 14, 95-101 (1942).
- ¹²² H. L. Bender, A. G. Farnham, and J. W. Guyer, U. S. pat. 2,464,217 (1950).
- ¹²³ H. L. Bender and A. G. Farnham, U. S. pat. 2,475,587 (1949).
- ¹²⁴ Bakelite, Ltd., Brit. pat. 592,278 (1947).
- ¹²⁵ Bakelite, Ltd., Brit. pat. 613,016 (1947).
- ¹²⁶ C. A. Buehler, D. E. Cooper, and E. O. Scrudder, *J. Org. Chem.*, 8, 316 (1943).
- ¹²⁷ S. R. Finn and J. W. G. Musty, *J. Soc. Chem. Ind.*, 1950, S49-S51.
- ¹²⁸ J. A. Arvin, U. S. pat. 2,463,501 (1949).
- ¹²⁹ E. G. K. Pritchett and G. Barnett, U. S. pat. 2,617,785 (1952).
- ¹³⁰ J. F. Walker and A. F. Chadwick, *Ind. Eng. Chem.*, 39, 974-977 (1947).
- ¹³¹ G. S. Petrox and T. V. Lokavenko, *Org. Chem. Ind. U.S.S.R.*, 3, 702-704 (1937).

¹³² J. W. Aylsworth, U. S. pat. 1,033,044 (1912).

¹³³ E. E. Novotny, U. S. pat. 1,767,696 (1930); U. S. pat. 1,849,109 (1932);
U. S. pat. 1,802,390 (1931).

¹³⁴ P. H. Rhodes, *Modern Plastics*, **22**, 160-161, 198 (1944).

¹³⁵ J. W. Aylsworth, U. S. pat. 1,020,593 (1912).

C H A P T E R F I V E

Cure of Phenolic Resins

One of the most valuable features of the phenolic resins is the ease and rapidity with which they may be converted to well-knit, highly cross-linked products. Commercial phenolic resins, as discussed in the previous chapter, are of two major types, the One-Stage resins, which contain the necessary functionality for cure in the form of an adequate number of reactive methylol groups, and the Two-Stage resins, which are made with a deficiency of formaldehyde and require an added curing agent.

In preparing a One-Stage resin it is common practice to carry the condensation reactions to a desired intermediate stage in the resin kettle. The reaction is then interrupted by lowering the temperature and possibly also by adjusting the *pH* of the system. Cure, which is here defined as the formation of an insoluble and infusible product, is effected by raising the temperature and by the addition of acidic reagents.

The Two-Stage resins, as previously discussed, require two steps, one for the preparation of the permanently soluble and fusible novolac resin and one for the addition of the curing agent which makes possible the conversion to a thermoset product. Cure of the Two-Stage resin is brought about by the application of heat in the presence of the curing agent. Hexamethylenetetramine is the most common curing agent, but others such as paraform have been used.

REQUIREMENTS FOR CURE

In order for cure of a One-Stage resin to result, the phenol and the aldehyde must be combined in the proper ratio and the system must possess adequate functionality. Since the functionality of formaldehyde is fixed at 2, the functionality of the phenol must be greater than 2 if cure is to result. Among the trifunctional phenols, phenol, *m*-cresol, and resorcinol are used in greatest volume for the manufacture of

thermosetting resins. Mixtures of tri- or tetrafunctional phenols with difunctional phenols will also give curing resins, and small amounts of monofunctional phenols may also be present without causing an undue sacrifice in curing properties.¹⁻⁴ The amount of tri- or tetrafunctional phenol necessary to maintain good curing properties varies widely with the phenol. Even when a trifunctional phenol is present in large amounts good cure may not result if the phenol carries bulky or negative substituents. On the other hand, certain phenols with a functionality of 2 or even 1, according to the definition given on page 11, may give cross-linked polymers.⁵⁻⁷ In such instances the additional functionality arises from sources not covered by the definition. This phase of the problem is discussed on page 146.

In order to take advantage of the polyfunctionality of the phenol in bringing about cure, more than 1 mole of formaldehyde, on the average, must be combined per mole of phenol.⁸⁻¹⁴ With a deficiency of combined formaldehyde a curing resin will not result regardless of the functionality of the phenol.* As soon as the molar ratio of combined formaldehyde to phenol exceeds 1 to 1, the possibility for cure results and reaches a maximum with phenol at a formaldehyde-to-phenol ratio of around 1.5:1, e.g. stoichiometric quantities, and declines somewhat on either side of this ratio. The physical properties of the cured resins also appear to reach a maximum at or near the 1.5:1 ratio. The decline in rate of cure above the 1.5:1 ratio is attributed to the lack of ring hydrogens with which the methylol groups may react. However, this does not prevent cure since the methylol groups can react with one another to form ether linkages. Also formaldehyde may be lost from a phenol alcohol and thus regenerate some reactive ring positions.

The requirements for cure of a Two-Stage resin are similar to those for a One-Stage resin. The novolac resin, which is the phenolic portion of the Two-Stage resin, contains at least $n + 1$ moles of combined phenol for n moles of combined formaldehyde. The formaldehyde appears in the form of methylene bridges linking together the phenol rings. In order for cure to result the novolac resin must be derived from a phenol, or mixture of phenols, with a functionality greater than

* Curing resins have been obtained in certain instances when less than a mole of formaldehyde was used per mole of phenol. In such instances part of the phenol has reacted with more than 1 mole of formaldehyde and the rest has failed to react at all. This, incidentally, is not uncommon. When such a resin is dehydrated, the unreacted phenol may be removed until the quantity of combined formaldehyde per mole of phenol in the residue will be greater than 1:1. The resin remaining will indeed cure.

2. Sufficient curing agent must be added to cross-link the novolac resin chains effectively. The total number of cross ties for each phenol nucleus must be greater than 1 to 1 and should approach the 1.5:1 ratio specified for the One-Stage resins. Of course, the methylene bridges already present in the novolac resin are counted in this calculation and reduce by that amount the quantity of curing agent required.

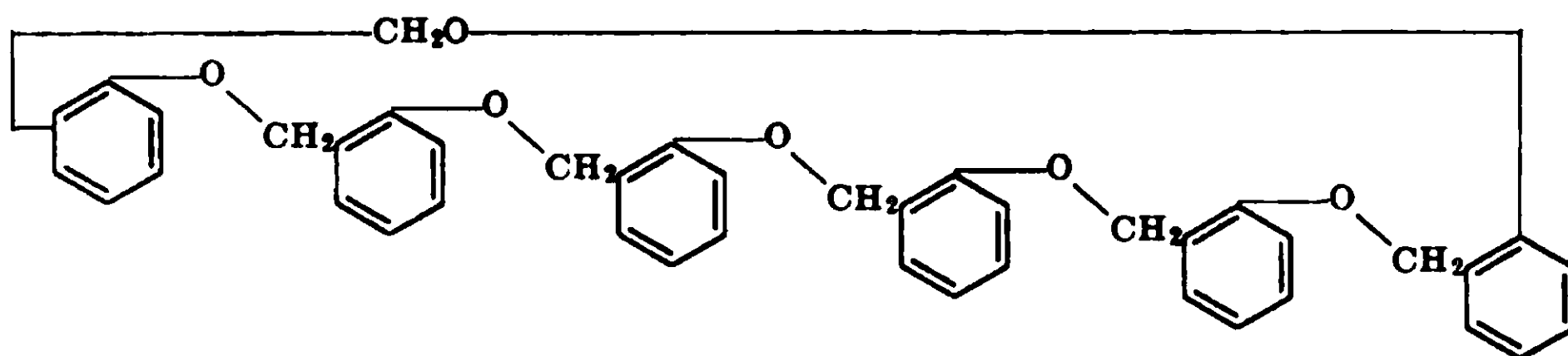
Although the essential requirements for cure of the One-Stage and the Two-Stage resins are similar, the reactions involved are quite different. For this reason the processes involved will be discussed separately. In addition the discussion of the cure of One-Stage resins will be further subdivided into that brought about by thermal means and that effected by catalysts, particularly acidic reagents which cause reaction at room temperature.

EARLY THEORIES ON CURE

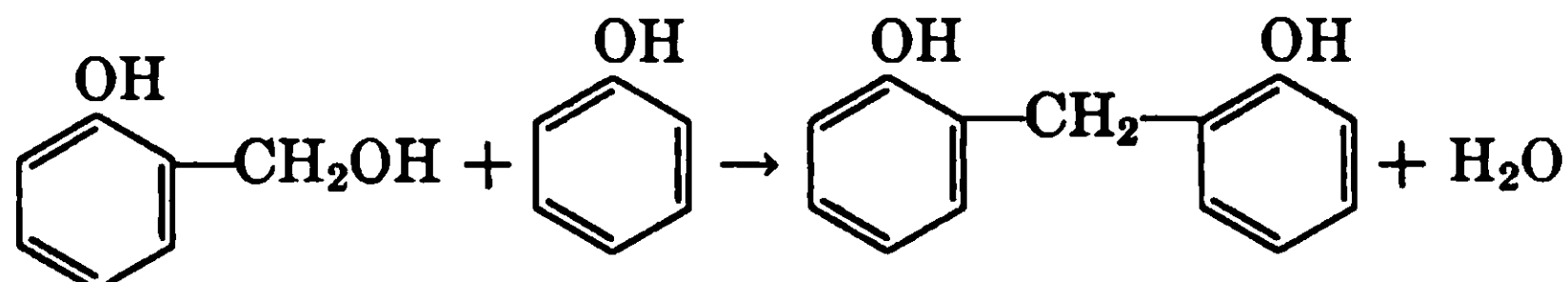
Before starting the discussion of the curing processes observed in phenolic resins a brief review of some of the early theories on the subject may be of interest.

Baekeland^{9,15} made an attempt about 1909 to classify the steps through which a resin passes in reaching the insoluble and infusible state. Without specifying in detail the nature of the reactions involved, phenolic resins were divided into three stages, A, B, and C, depending on their degree of condensation. Lebach^{16,17} made a similar division of the products into resoles, resitols, and resites. This classification roughly parallels that of Baekeland, but a more detailed picture of the resin at each stage was given. In the A or resole stage the resin is both soluble and fusible. The term "resole" was coined by Lebach from the Latin *resina*, which means "resinous body," and "ol," because of the solubility of the resin in alcohols and probable presence of hydroxyl groups. The resin at the B or resitol stage is still fusible but is no longer soluble in alkalies and may be only partially soluble in solvents such as acetone. In the final C or resite stage the resin is insoluble even in strong solvents and does not melt below the point of decomposition. Although the various stages were ill defined, speculations were made very early as to the reactions involved in going from one stage to another.

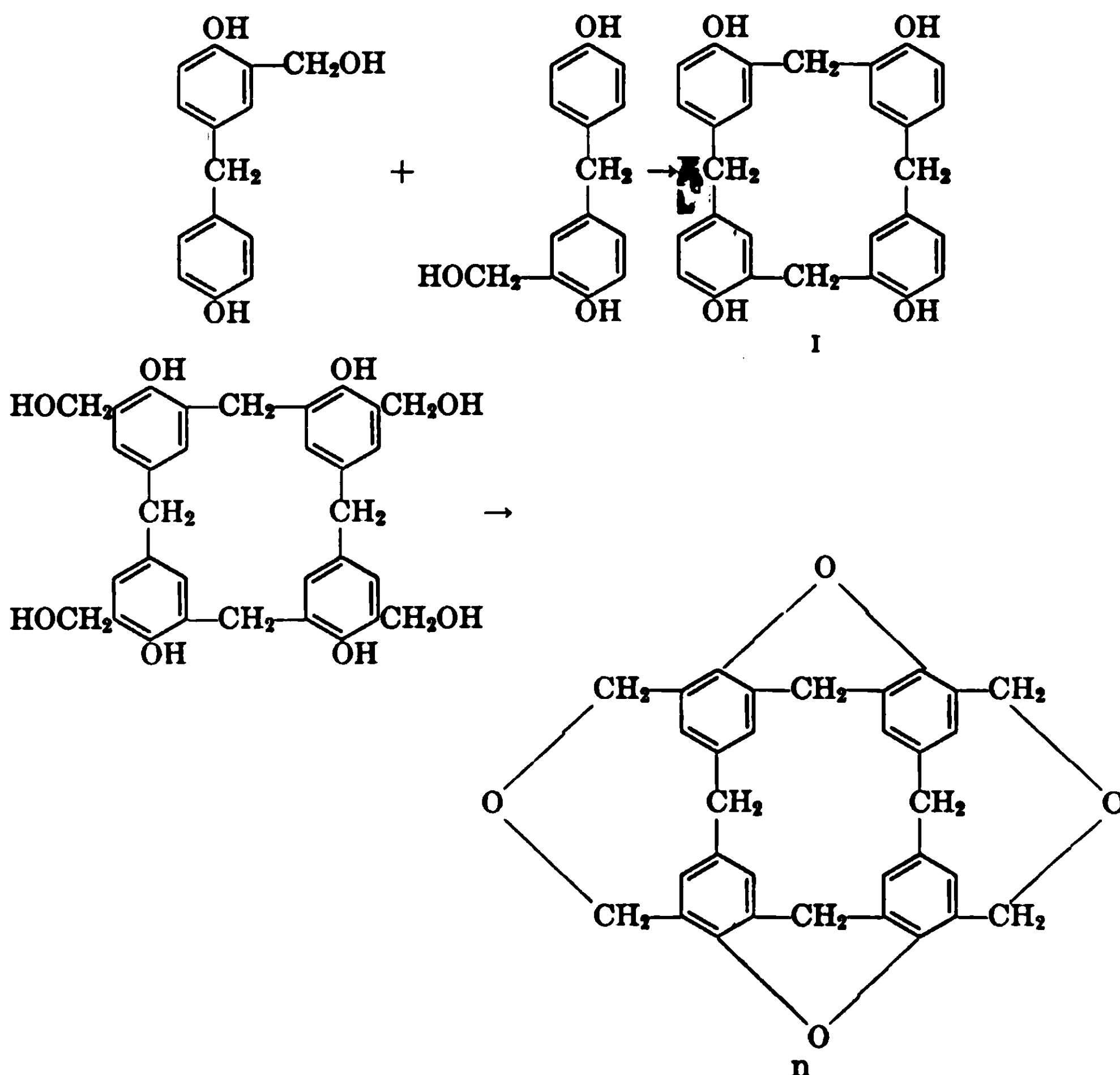
Baekeland^{18,19} proposed around 1909 the formation of ether linkages in the resinification processes. Since the addition of 1 mole of formaldehyde for each 6 moles of saligenin was required for cure, the following structure for the resin was suggested:



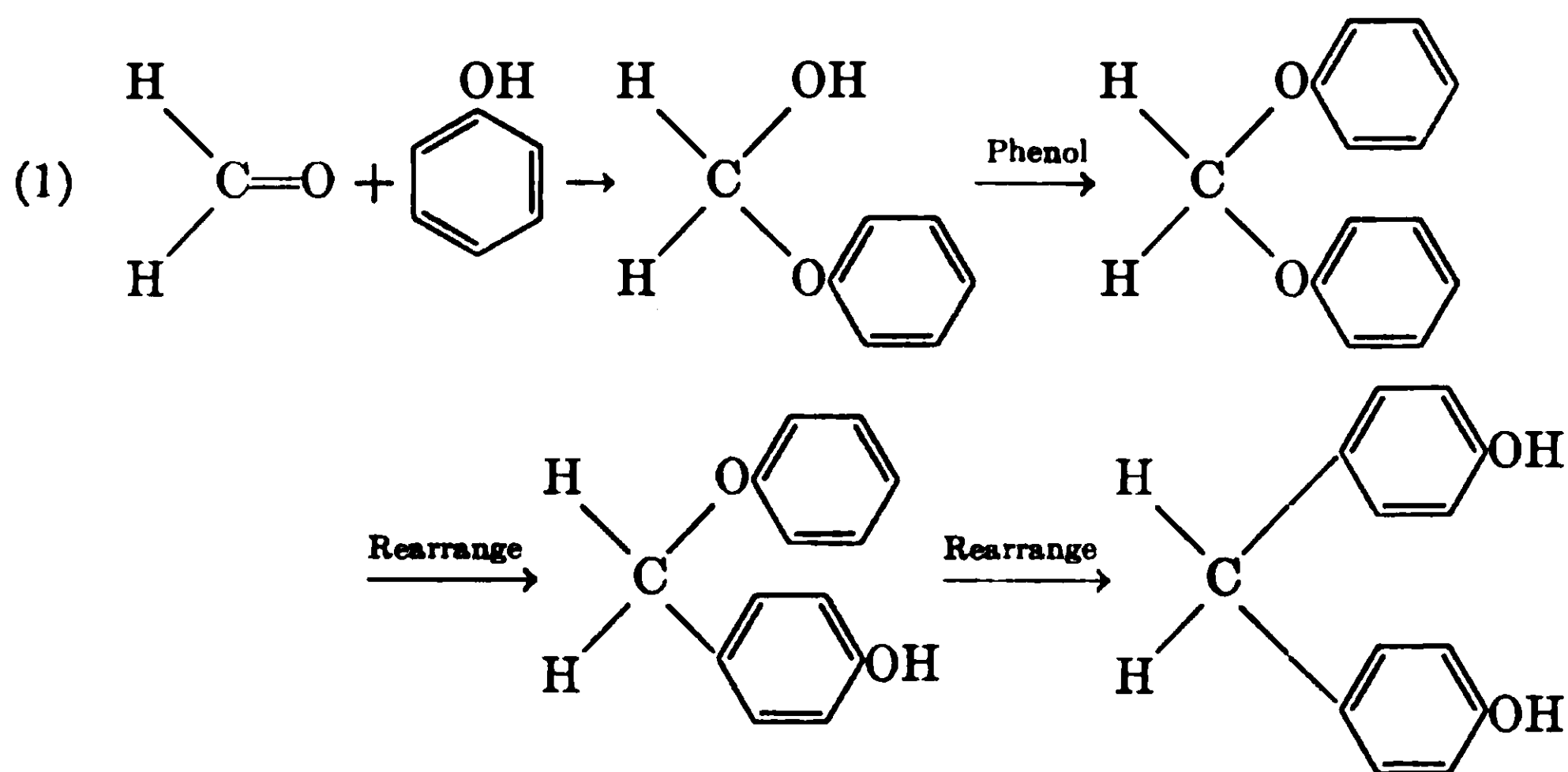
Some three years later Raschig^{19,20} suggested the formation of methylene derivatives:



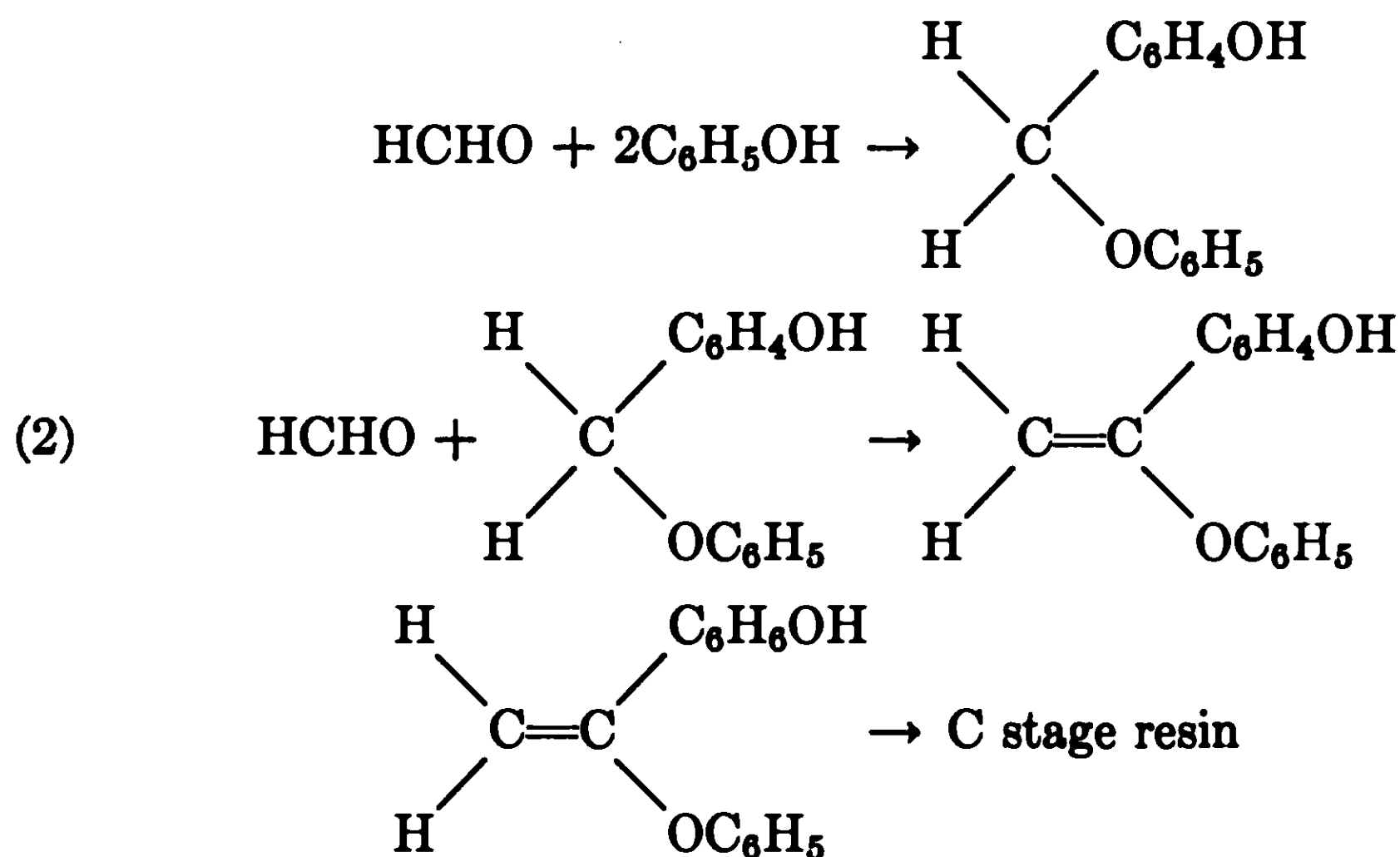
When the phenol and formaldehyde were used in roughly equivalent amounts Raschig visualized that Bakelite I, formula I, was formed. With higher ratios of formaldehyde compounds carrying methylol groups might result which on further condensation could form Bakelite II, formula II.



When it was found that dihydroxydiphenylmethanes could be isolated from low-stage phenolic resins, Baekeland and Bender revised Baekeland's ether theory and proposed that the ethers might serve as intermediates for the formation of the dihydroxydiphenylmethanes.²¹ The reactions proposed are shown below in reaction 1. These authors

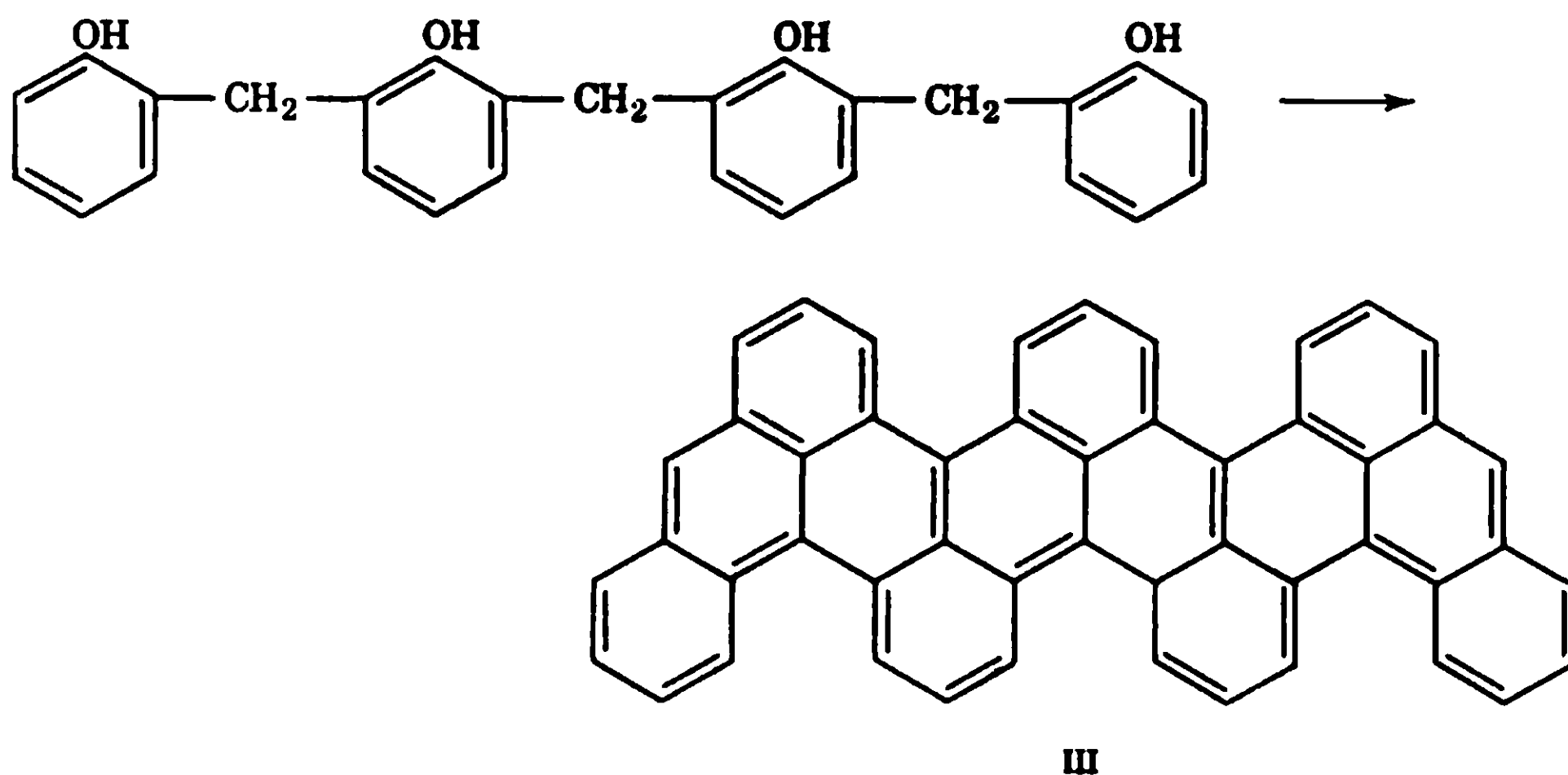


went on to suggest that the final C stage resin might be the result of polymerization reactions. The various steps are shown in equation 2.



A highly idealized picture, now considered untenable, for a cured resin was given by Blumfeldt.²² According to Blumfeldt, Bakelite C, formula III, may be obtained by the condensation of two chains with *ortho*-methylenes such as might be found in certain novolac resins. Since the methylene bridges may also be attached at the *p*-position

in the intermediate polynuclear methylene derivative, the possible formation of other condensation products besides III, which has a polynuclear aromatic structure, was granted.



Of these early theories those of Raschig most nearly represent our modern concepts. With the help of such men as Koebner,²³⁻²⁵ Barthel,²⁶ and Megson,²⁷⁻³¹ and others a workable picture of phenolic resins and of cure was developed. However, many of the details were still missing. Beginning around 1940 three groups of workers in Europe, Hultzsich at the Kurt Albert Corp. in Wiesbaden, Zinke, Ziegler, and Zigeuner at the University of Graz, and Adler and von Euler at the University of Stockholm, with the help of their collaborators, set about to fill in the details and learn more about the many complex transitions that may occur on heating a phenolic resin. Megson, Finn, and Musty and Hunter and Carpenter in England and Imoto, Seto, and Tsurata in Japan were also active during this period. In America major contributions were made by Sprung, Nordlander, Bender, Sprengling, Freeman, Lewis, Granger, and many others.

A. THERMAL CURE OF ONE-STAGE RESINS

Unlike many polymeric systems where cure results by repetition of a single process, the cure of a phenolic resin is extremely complex, involving as it does a number of competing reactions each of which may be profoundly influenced by reaction conditions and the structure of the phenol used to prepare the resin. A further complicating factor is introduced by the possibility of reaction at either or both the *ortho* and *para* positions of the phenol. This leads not only to the formation of a large number of isomeric products but also to products of

varying reactivity, depending on the location of the functional group. In view of the complexity of the system it is not surprising that knowledge of the curing processes fell far behind the commercial development of phenolic resins.

Major strides were made in clarifying the mechanism of cure only when methods were developed for simplifying the systems. This was achieved by using pure phenol alcohols in place of the complex mixtures found in typical resins. This approach is fundamentally sound since it is now accepted that functional groups, in general, undergo the same reactions in monomeric and polymeric systems.³² Further, it has been claimed, in certain systems at least, that reactivity on a molar basis remains essentially unchanged as the molecular weight is increased.³³

Although much was learned from the studies with pure phenol alcohols, the technique was criticized since *ortho*- and *para*-substituted phenol alcohols generally were employed at first. It was claimed by the critics of the method that a substituent in a potentially reactive *ortho* or *para* position may promote certain reactions of the phenol alcohols and hinder others which might occur if the substituent were absent. This criticism has since been met by studies with phenol alcohols derived from trifunctional phenols.

The studies with phenol alcohols have revealed among other things that the nature of the reactions is dependent on temperature.^{4, 34-38} Below about 170°C., reactions characterized primarily by molecular enlargement predominate. The primary reactions in this temperature range are: (a) those wherein a methylol group of one phenolic body reacts, by elimination of water, with an *ortho* or *para* ring hydrogen of another phenolic body to form a methylene bridge, and (b) those wherein two methylol groups react with each other, also with the elimination of water, to form a dibenzyl ether linkage. Formaldehyde also may be regenerated from a methylol group below about 170°. A dibenzyl ether linkage likewise may be converted to a methylene bridge by loss of formaldehyde or by reaction with a ring hydrogen of another phenolic body through the loss of water. However, these reactions are of minor importance compared to the two mentioned above.

The second phase of the purely thermal reaction of a phenol alcohol starts around 160–170°C. but may not become extensive until a temperature as high as 200°C. is reached. Many of the reactions in this temperature range arise from further reactions of dibenzyl ethers and occasionally from a phenol alcohol that has not already reacted at a lower temperature. The reactions are characterized by little or no loss

of formaldehyde and frequently involve no loss of water.^{37, 39} They are accompanied by a strong brown or reddish brown discoloration of the resin and involve the formation of quinone methides and their polymerization and oxidation-reduction products along with aldehyde and methyl end groups. It is also possible that the quinone methides may result from loss of phenol from the end of a resin chain.⁴⁰ The reactions in this temperature range are frequently accompanied by a decrease in hydroxyl content and a decrease in molecular weight of the resin although the molecular weight may again increase after the initial drop.^{33, 41-43} These more or less deep-seated changes are of little importance to the cure of commercial resins, although they may be involved in their high-temperature aging.

Figure 3 outlines a number of the thermal reactions that have been discovered as a result of studies with phenol alcohols. An effort has been made to arrange the reactions in the chart so that a separation into those occurring below about 160–170°C., the first phase, and those occurring at higher temperatures, the second phase, may be visualized. This separation has been made on a more or less arbitrary basis, and some overlapping obviously occurs. Similar diagrams have been published elsewhere.^{4, 44} Any such diagram only serves to emphasize why a clear-cut description of the thermal curing processes, applicable to all types of resins under varying curing conditions, cannot be given. In an effort to simplify the discussion, the various reactions are considered separately, although this seldom, if ever, occurs in practice.

Methylene Bridge Formation

The methylene bridge is the most stable as well as the most important linkage established during the cure of a phenolic resin. It may be formed either directly or indirectly. The most important direct means is by elimination of water between a methylol group of one phenolic body and an *ortho* or *para* ring hydrogen of another phenolic body. The mechanism for this reaction has already been discussed (see page 48). According to Imoto and Kimura,⁴⁵ the heat of activation for methylene bridge formation is 13.7 kcal./mole.

A *para* methylol group appears to be somewhat more susceptible to conversion to a methylene bridge than an *ortho* methylol group.^{45a} This explains the high proportion of *para* methylene derivatives found during the early stages of resinification. As the resinification proceeds the *para* methylols will be consumed, leaving mainly the *ortho* methylols available to bring about a major part of the final cure of the resin.^{4, 46}

Besides the location of the methylol group, the structure of the parent phenol may affect cure rate. In general, those phenols that react readily with formaldehyde give resins that cure well provided that steric factors do not interfere. An example of the adverse effect

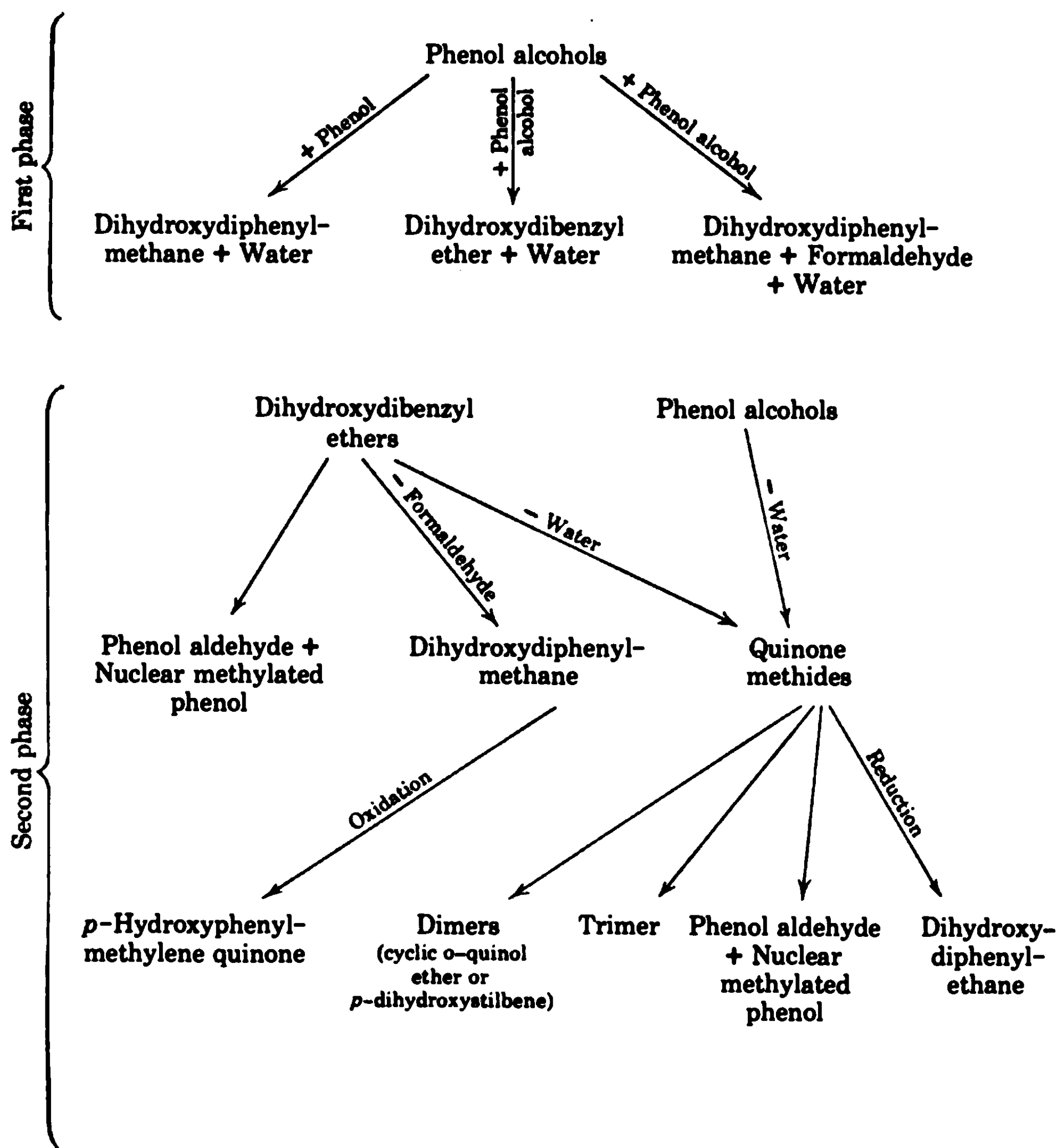


Fig. 3. Hardening of phenol alcohols.

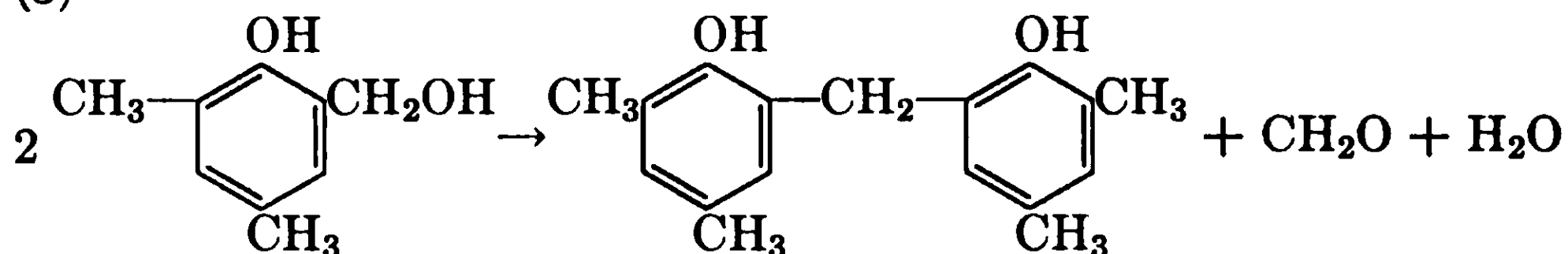
of the substituents on a highly reactive phenol is found in 3,5-xyleneol. According to Sprung,⁴⁷ this phenol reacts with formaldehyde during the early stages of reaction at a rate roughly eight times that of phenol. However, it is surprising to find that the reaction essentially stops with the addition of 2 moles of formaldehyde.⁴⁸ Steric factors have been blamed for this as well as for the fact that 3,5-xyleneol, even when combined with 2 moles of formaldehyde, which should be adequate for cure, forms resins that do not show outstanding cure.⁴⁹ In spite of

its rather poor curing properties when used alone, 3,5-xyleneol is useful as a scavenger to pick up small amounts of formaldehyde if added to a resin just before dehydration. It will also increase the speed of cure of One-Stage resins if added in small amounts (5–15%) just before cure.⁵⁰ Other highly reactive phenols, such as resorcinol, are employed in a similar capacity.⁵¹

Both alkalies and acids have a favorable effect in catalyzing the formation of methylene bridges.^{45a} With acids at moderate temperatures the rate is roughly proportional to the hydrogen-ion concentration of the reaction mixture, but with strong alkalies the rate, in the early part of the reaction, is independent of the alkali concentration above a certain minimum figure.^{52–55} The last fact, though reported by several workers, is frequently overlooked by resin chemists. From data published by Müller and Müller⁵⁴ and Vanscheidt and Vasiliev⁵⁵ it appears that the cation also has some effect on the rate of condensation in a phenolic resin.

Methylene bridges may be formed not only by the reaction discussed above but by certain other means as well. An important means is by reaction of 2 moles of a phenol alcohol whereby a mole of formaldehyde and a mole of water are eliminated, reaction 3. Both

(3)



acidic and alkaline catalysts and a high ratio of combined formaldehyde to phenol in the resin favor the reaction. High temperatures also favor the reaction. Phenol monoalcohols having no active hydrogens are particularly susceptible to the reaction.^{56–58} *p*-Hydroxybenzyl alcohol, 2,4-dimethylolphenol and trimethylolphenol also undergo this reaction.^{45a}

Since the formation of phenol alcohols is basically an aldol type of reaction, Hultsch⁴ contends that either an increase in temperature or a lowering of the *pH* of the system should tend to reverse the reaction and make the escape of formaldehyde possible. Hultsch suggests that, at the moment the formaldehyde is released the free phenol would be in an active state and thus very susceptible to reaction with a phenol alcohol.

It should be reported, however, that the phenol formed by the loss of formaldehyde from a phenol alcohol does not always combine immediately with a phenol alcohol to form a dihydroxydiphenylmethane.

This has been demonstrated by the removal of free phenol by steam distillation of a solution of a phenol alcohol that has been acidified.⁵⁹ The loss of formaldehyde from trimethylolphenol following acidification also has been reported.^{45a, 60} Phenol alcohols with less than three methylol groups also have been separated from the reaction mixture.⁶¹ The liberation of formaldehyde from a phenol alcohol by reversal of the addition reaction would not be too surprising in view of the findings in other systems.⁵⁹⁻⁶⁵ Both mono- and dimethylolurea are in dynamic equilibrium with formaldehyde and urea. Furthermore, the point of equilibrium may be approached from either direction and is essentially independent of catalysts.^{62, 64}

The loss of formaldehyde from a phenol alcohol under alkaline conditions is not strictly analogous to that which occurs by the action of heat or acids.^{56, 65} It is pictured as an ionic reaction in which the methylol group is displaced simultaneously with the formation of the methylene bridge (see page 92).

Apparently both the structure of the phenol alcohol and reaction conditions are important factors in determining whether and to what extent the reaction may occur. For example, *p*-cresol dialcohol behaves differently in aqueous solution and in a melt. No loss of formaldehyde was detected by DeJong and DeJonge^{64, 65} when the dialcohol was heated to 90°C. in aqueous solution for 5 hours with *pH* held at 8 or in 2 hours with *pH* held at 11. On the other hand Kammerer^{66, 67} reports that formaldehyde was evolved when *p*-cresol dialcohol was heated in a melt in the presence of sodium ions. When all sodium ions were removed the evolution of formaldehyde ceased. Contrasted to the stability of *p*-cresol dialcohol in aqueous caustic even at elevated temperature is the instability of trimethylolphenol. Trimethylolphenol lost formaldehyde slowly at room temperature when stored for several months as a 1 *N* solution.⁶¹ When present as a sodium salt, trimethylolphenol is converted to tetramethyloldihydroxydiphenylmethane quite rapidly in aqueous solution. (Ehlers⁶⁶ claims that phenol alcohols form complexes with sodium and that these complexes influence cure.)

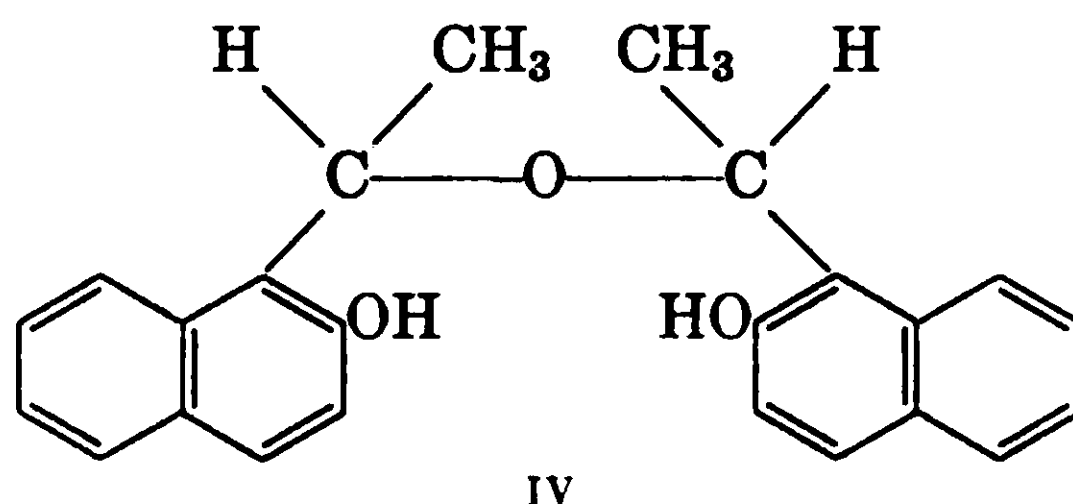
Methylene bridges also may be formed indirectly by loss of formaldehyde from a dibenzyl ether linkage (see page 62).

Dibenzyl Ethers

Ether formation proceeds readily with most, if not all, benzyl-type alcohols. Therefore it is not surprising that the reaction can play an important role in the cure or hardening of certain types of phenolic resins. The surprising part is that its importance was discovered so

recently. Besides the reaction between two methylol groups, ethers may be formed by reaction of a phenol alcohol with a chloromethylphenol⁶⁹ or an aliphatic alcohol. The products of the latter reaction are known as the alkoxymethylphenols. Greth⁷⁰ used the reaction of aliphatic alcohols with methylolphenols to prepare modified phenolic resins soluble in hydrocarbon solvents. A similar procedure is widely used with melamine and urea resins to improve their solubility and compatibility with alkyd resins and thinners. Butyl alcohol has been found particularly suitable for this purpose with both the amine and phenolic resins. In general the formation and frequently the reactions of the alkoxymethylphenols are similar to those of the dihydroxydibenzyl ethers, although their reactivity may be reduced.

In addition to the ethers derived from unsubstituted benzyl alcohols examples are known where ethers of substituted benzyl alcohols have been formed such as the compound IV.⁷¹

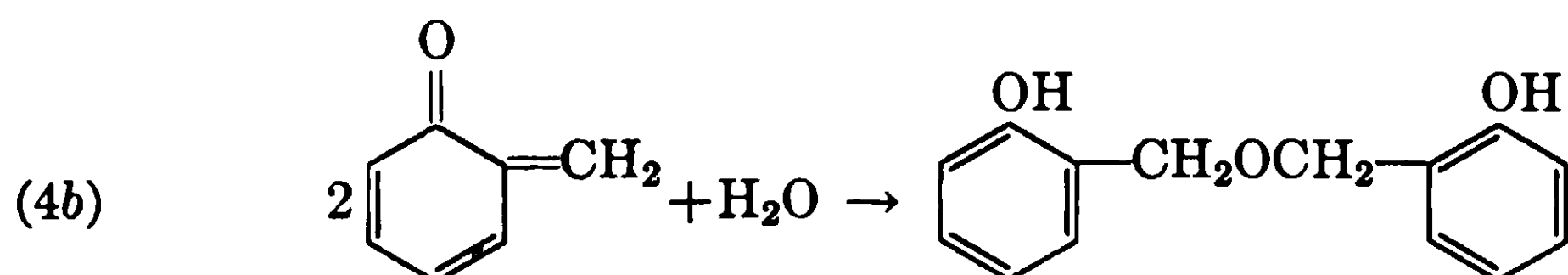
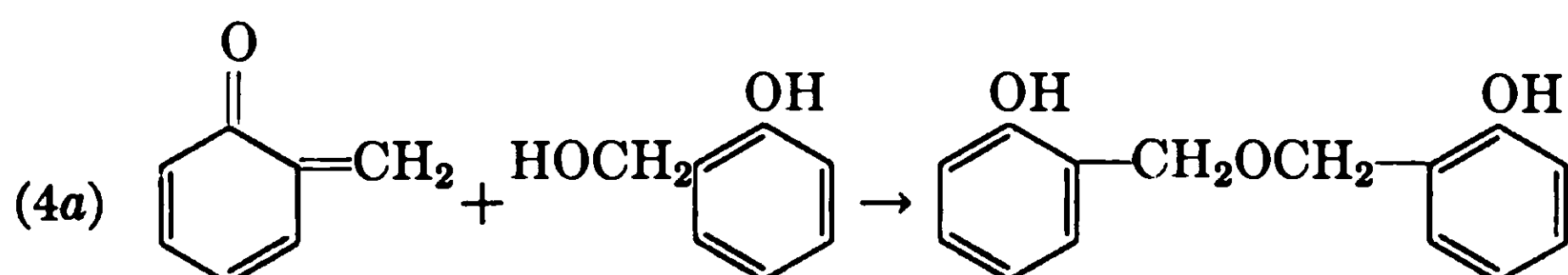


According to Imoto and Kimura⁴⁵ the heat of activation for formation of the ether linkage is 27.4 kcal./mole.

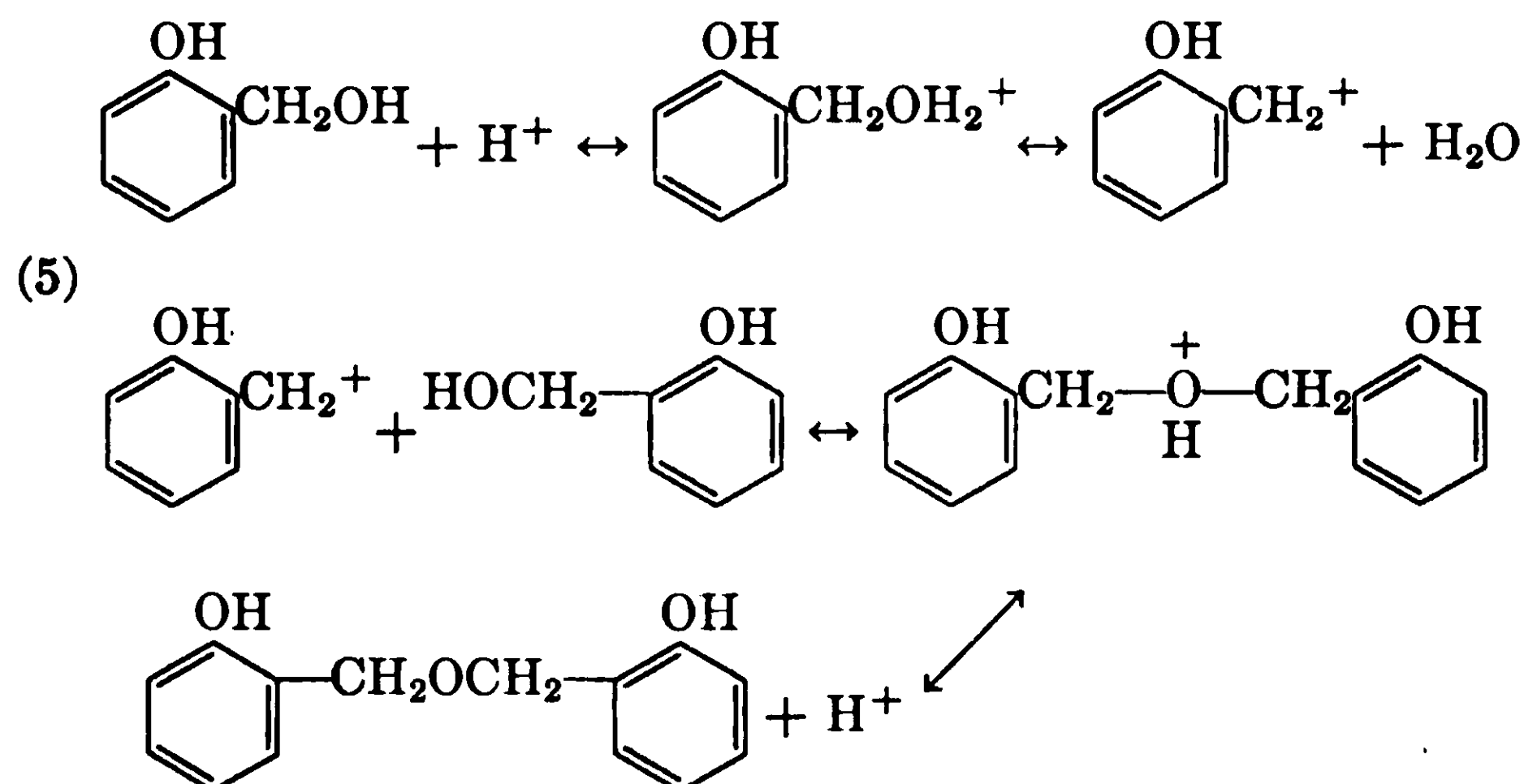
The dihydroxydibenzyl ethers play a dual role in phenolic resin chemistry since they may function both as transition and as end products. The ease of formation as well as the tendency of the dibenzyl ether linkage to undergo further reactions, which will be discussed later, depends on the substituents attached to the benzene ring.⁷² Benzyl alcohol, having no substituents, may be distilled essentially unchanged if acids are carefully excluded. Methoxybenzyl alcohols also show reasonable stability. The dimethyl ether of dimethylolhydroquinone is stable at 180°C., and the monomethyl ether of *p*-cresol dialcohol is essentially unchanged after heating 1 hour at 160°C.^{73,74} All these benzyl alcohols and others of similar structure form ethers readily when heated with small amounts of acids.⁷² On the other hand, *o*- and *p*-hydroxybenzyl alcohols are activated to such an extent by the phenolic hydroxyl group that ethers can be formed from them without the addition of catalysts, although here, too, acidic catalysts in very small amounts are sometimes beneficial with phenol alcohols of low reactivity.^{45, 45a} The more active phenol alcohols may be con-

verted to dihydroxydibenzyl ethers at temperatures as low as 70° to 100°C. in a neutral or acidic aqueous medium and at 80° to 100°C. in a resin melt.^{4, 45a} With inactive phenol alcohols, temperatures between 140° and 170°C., may be required. Under special conditions, ethers also may be formed even at room temperature.^{69, 75} Apparently the benzyl alcohols obtained by esterification of the phenolic hydroxyl group of a phenol alcohol fall between benzyl alcohol and the phenol alcohols in activity, the tosyl ester appearing more reactive than the acetate esters.⁷⁴ Tetramethylolquinone also forms polyethers on heating.

Two mechanisms have been proposed to explain the formation of the dibenzyl ethers. The first mechanism involves either the addition of 1 mole of a phenol alcohol to 1 mole of a quinone methide, reaction 4a, or the addition of 2 moles of the quinone methide to 1 mole of water, reaction 4b. The driving force for either reaction, both of which have been proposed by Hultzsche,⁴ would be derived from the ease with which a phenol alcohol may lose water to form a quinone methide.



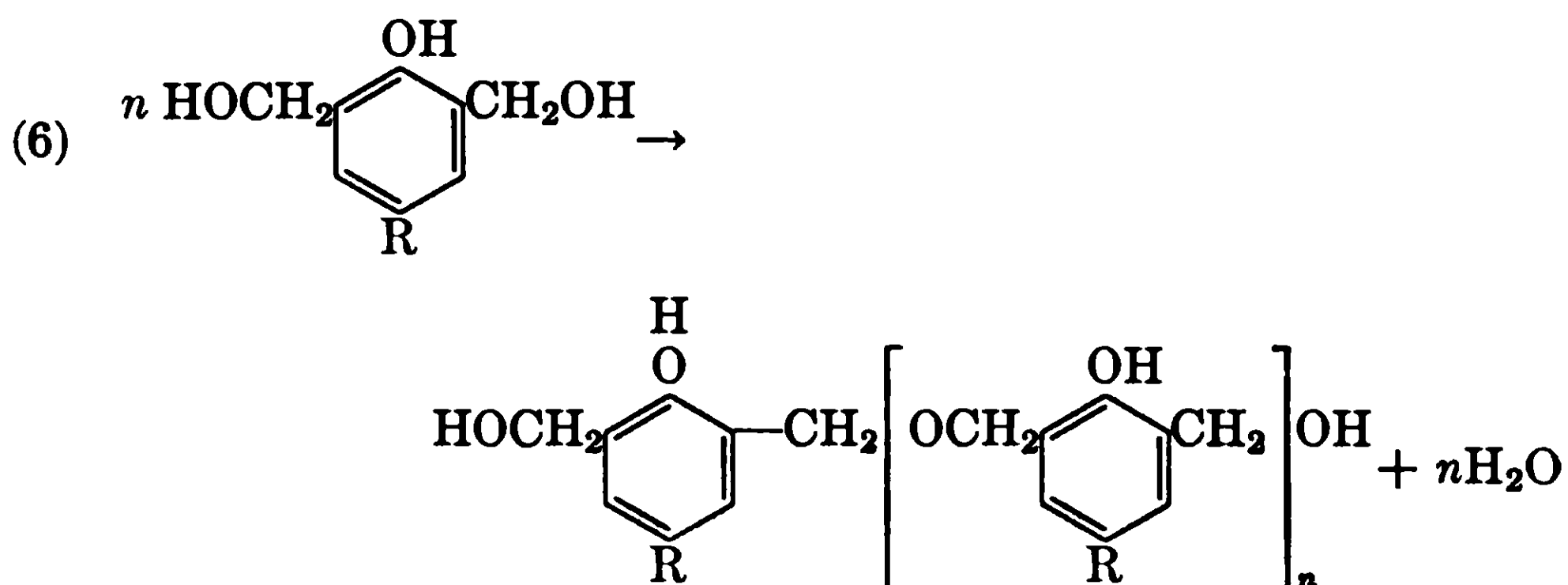
The ionic type of mechanism shown in equation 5 was suggested by Lilley.⁷⁶ Hultzsche later concluded that this mechanism may be



more probable than the one attributed to him earlier. The present author also favors Lilley's mechanism.

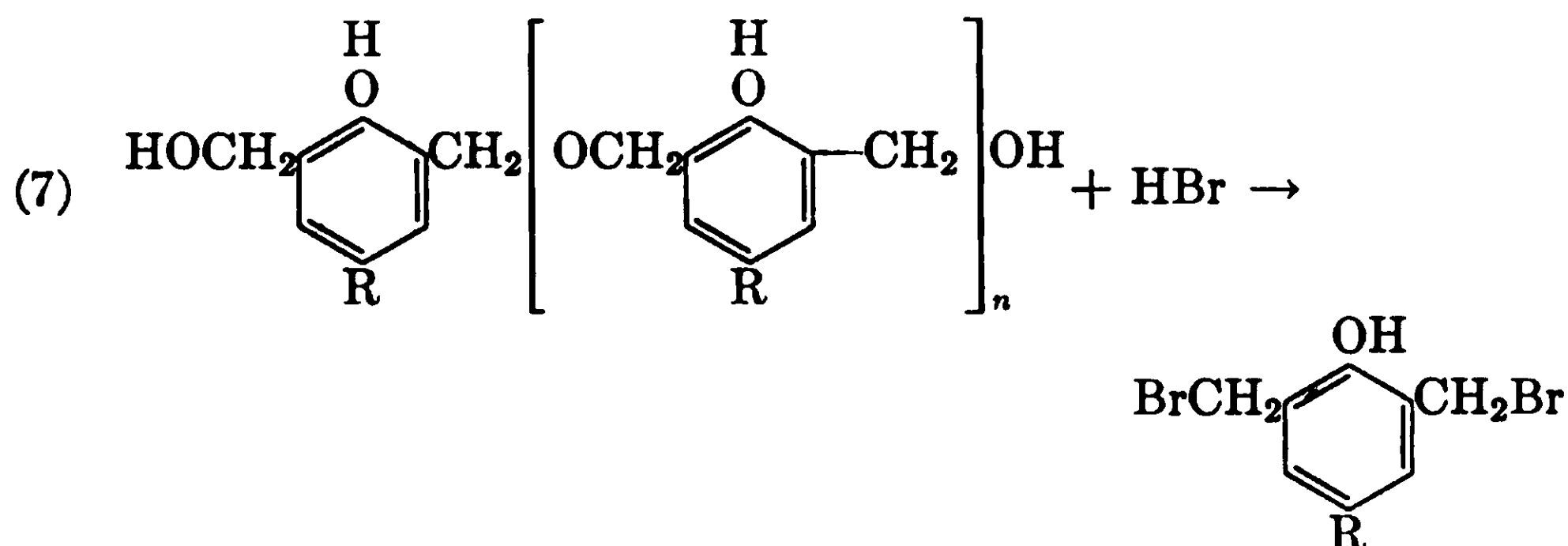
Giocasa⁷⁷ probably obtained one of the first dihydroxydibenzyl ethers when he heated saligenin in a sealed tube with glycerine. He separated a small quantity of a crystalline compound, m.p. 121.5°, which he called salireton. He felt that he had effected condensation between saligenin and *o*-hydroxybenzaldehyde (formed by oxidation of a portion of the saligenin). The structure of Giocasa's compound, frequently mentioned in the early literature, was not established until 1941, when Ziegler and Lercher⁷⁸ found it to be 2,2'-dihydroxydibenzyl ether.

The classical studies of Auwers⁷⁹⁻⁸¹ some 20-30 years after Giocasa's work provide much of our basic information concerning hydroxybenzyl ethers. However, Auwers failed to associate ether formation with the cure of phenolic resins. Zinke, Hanus, and Ziegler⁸² and Hanus and Fuchs⁸³ were among the first to demonstrate this point. These authors prepared a number of *p*-alkyl phenol dialcohols and converted the compounds to resins by heating above their melting points. Water was evolved, and linear polymeric ethers were formed; reaction 6.



p-Cresol dialcohol gave polymers with as many as 35 units per chain.⁸⁴ The presence of the ether linkages was demonstrated by treating the polymers with hydrogen bromide. This treatment degraded the polymer and formed bromomethylphenols identical with those obtained by treatment of the parent phenol alcohols with hydrogen bromide, reaction 7. By an extension of this technique it has been possible to follow the ether content of a resin as condensation proceeds. The resin is first treated with hydrogen bromide, and the bromine content of the treated product is then determined.^{84, 88, 85, 88}

Hanus and Fuchs⁸⁸ also made the interesting observation that the temperature at which water was lost and ether formation set in was



strongly influenced by the size and nature of the *para* substituent. At some higher temperature, also varying with the substituent, the polyethers became unstable and evolved formaldehyde. Table I,

Table I

<i>para</i> Substituent	Temperature at which Water Is Split Off, °C.	Temperature at which CH ₂ O Is Split Off, °C.	Difference, °C.
Methyl	135	145	10
Ethyl	130	150	20
Propyl	130	155	25
<i>n</i> -Butyl	130	150	20
<i>t</i> -Butyl	110	140	30
Phenyl	125	170	45
Cyclohexyl	130	180	50
Benzyl	125	170	45

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taken from the paper by Hanus and Fuchs, shows the effect of the *para* substituent on the temperature of onset of the two reactions. Hanus and Lercher⁸⁷ made a similar study of the effect of an *ortho* alkyl substituent on the loss of water and formaldehyde. They found that the effect of the alkyl group was not as great or as sharply defined as it was with the *para*-substituted dialcohols.

In general the dinuclear phenol dialcohols form ethers which show much less tendency towards the loss of formaldehyde than those derived from mononuclear phenol alcohols. The same is true for the trinuclear phenol dialcohols. However, most polynuclear phenol alcohols lose some formaldehyde if the temperature is raised high enough. Further, the loss of water does not necessarily stop at 1 mole per mole of dialcohol. For example, Kyrning⁸⁸ found that at 130° or 200°C. the dialcohol from the trinuclear derivative of *p*-cresol lost almost ex-

actly 1 mole of water for each mole of dialcohol, indicating almost exclusive ether formation. However, at 240°C. water continued to split out until 1.85 moles per mole of dialcohol was lost.

As mentioned previously, much criticism was leveled at this early work since phenol alcohols devoid of reactive ring positions had been used. The critics contended that the results might not be applicable to commercial resins, many of which are based either on phenols which carry no substituents or on other trifunctional phenols with substituents only at the *meta* positions. In either event the resins would have free *ortho* and *para* positions available for reaction.

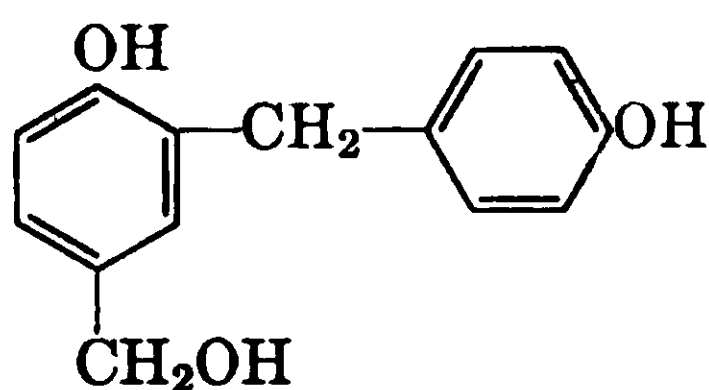
In an effort to overcome the above criticisms, studies were undertaken of the reactions of phenol alcohols having reactive *ortho* and *para* hydrogens. Saligenin, for example, which has both a free *ortho* and *para* position, forms 2,2'-dihydroxydibenzyl ether (salireton) when heated under neutral conditions. In Giocasa's experiments only a 2% yield of the ether was obtained, but it has now been found that yields ranging upwards to around 80% of the theoretical amount are possible.^{58,77,78} Sprung has made a detailed study of the condensation of this compound alone and with other phenols.⁸³ In the absence of a catalyst and other phenols the predominant reaction is the formation of the dihydroxydibenzyl ether. The ether may also be formed under mildly acidic conditions but could not be detected under alkaline conditions. *p*-Cresol monoalcohol also forms a substantial yield of dibenzyl ether when heated under neutral conditions. The only product isolated on heating the monoalcohol of dihydroxytolylmethane was the corresponding dibenzyl ether (81% yield).^{73,89,90}

All the examples cited above were of phenol alcohols having only *ortho* methylol groups, and only one derivative of phenol, saligenin, had been studied. Therefore more data were needed on the phenol alcohols, other than saligenin, that might be found in a One-Stage resin based on phenol before the over-all importance of ether formation to the cure of such resins could be established. Reese^{48a} has made by far the most definitive study of this problem. He heated each of the five possible mononuclear phenol alcohols of phenol at 110°C. in a melt and at 70°C. under alkaline and acidic (aqueous) conditions for varying lengths of time. The products of the reaction were then separated by two-dimensional chromatography and their identity was either established or a structure was postulated for them on the basis of their R_f values.

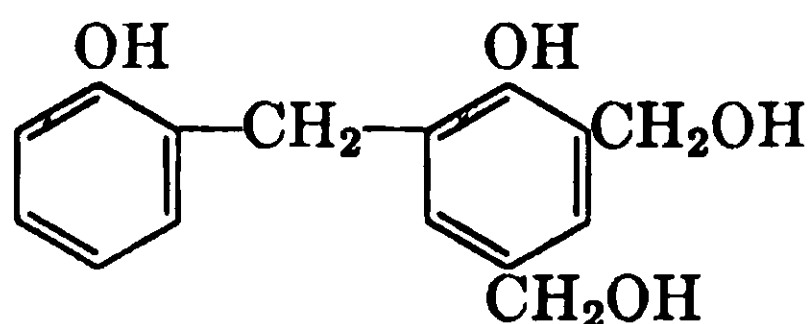
Just as Sprung⁸⁸ had found with saligenin, Reese found that none of the phenol alcohols were converted to ethers under alkaline conditions. On the other hand all five of the phenol alcohols formed

dibenzyl ethers in a melt. With saligenin, 2,6-dimethylolphenol, and trimethylolphenol the ether derivatives were major products. In contrast to this, appreciable quantities of the methylene derivatives were formed from *p*-hydroxybenzyl alcohol and 2,4-dimethylolphenol. Even under acidic conditions saligenin and trimethylolphenol formed some of the ether derivative.

Several polynuclear phenol alcohols that might be found in a One-Stage resin, such as V and VI, have been synthesized.^{91,91a} A study of their behavior in a manner similar to that employed by Reese would be helpful in extending our knowledge to some of the more complex molecules found in resoles. However, it seems unlikely that they will act very differently from the many compounds already studied.^{92,97}



V



VI

From the data now available several generalizations can be made as to the effect of *pH*, structure of the phenol alcohol, methylol content of the resin, reaction temperature, etc., on the formation of dibenzyl ether linkages. Although certain exceptions and refinements will undoubtedly be found as more studies are made the generalizations that follow will serve as a guide to what may reasonably be expected under a given set of conditions.

Under essentially neutral conditions, which will be assumed in a melt, ether formation has long been considered to be of major importance in the condensation of phenol alcohols derived from *ortho*- and *para*-alkylphenols. Sprung⁹³ and Reese^{45a} have found that the reaction is also important for phenol alcohols from trifunctional phenols.

As a rule acids in large amounts favor the formation of methylene derivatives and hence decrease the yield of dibenzyl ethers. However, small amounts of acids may accelerate ether formation where inactive phenol alcohols are involved. As mentioned above, some ether linkages were established when saligenin and trimethylolphenol were condensed under acidic conditions. Thus it appears that acidic conditions, though ordinarily not as favorable as neutral conditions, do not preclude, and may actually accelerate, the formation of dibenzyl ethers. Pritchett⁹⁸ thinks that wood adhesives made with a

high ratio of formaldehyde to phenol and cured near room temperature with acids may contain ether linkages.

Ether formation is essentially, if not completely, eliminated under alkaline conditions. This applies both to the phenol alcohols derived from phenol and those from *ortho*- and *para*-substituted phenols. Further it has been observed that certain dihydroxydibenzyl ethers are readily converted to methylene derivatives by heating in the presence of caustic.^{41, 95-97} These data indicate that the dibenzyl ether linkage, even if formed, is not stable under alkaline conditions.


Several structural features also appear to have an effect on the extent of ether formation. *Para*- and to a lesser extent *ortho*-alkyl-phenol dialcohols show a strong tendency to form dibenzyl ether derivatives on heating. Phenol dialcohols of *ortho*- and *para*-halogenated phenols behave similarly. Among the phenol alcohols derived from phenol, saligenin, *o,o*-dimethylolphenol, and trimethylolphenol give the highest yield of ether. From this it appears that phenols with *ortho*-methylol groups are generally more susceptible to ether formation than those with *para*-methylol groups. So far ether formation has not been demonstrated either in the formation or cure of such highly reactive phenols as resorcinol.

Lilley⁷⁶ has made a study of the effect of certain substituents on the relative tendency for a phenol alcohol to form a methylene or a dibenzyl ether derivative when either product is possible. *p*-Nitro- and *p*-chlorosaligenin were used for this study. The compounds were heated at 130° and 140°C. for periods ranging from 1 to 4 hours, and the amount of ether formed was estimated by the procedure of Lilley and Osmond.⁹² The *p*-nitrosaligenin gave a much higher yield of ether than the *p*-chloro compound.

In the thermal hardening of commercial One-Stage resins it is generally accepted that methylene and ether linkages are formed simultaneously.⁷⁸ Besides those factors already discussed the ratio of methylene to dibenzyl ether linkages formed depends on the number of methylol groups as compared to the number of free ring positions in the resin. With a resin of high methylol content or conversely with a resin with few free *ortho* and *para* ring positions ether formation becomes increasingly important.⁹⁸ Euler⁷⁸ has demonstrated this point by means of model compounds. The addition of phenols having reactive ring positions to phenol alcohols before heating decreased the amount of ether formation.

The effect of reaction temperature on the yield of dibenzyl ether cannot be accurately defined at this point. As mentioned earlier, Hanus and Fuchs⁸⁸ found that ether formation occurred at tempera-

Table II. Dihydroxydibenzyl Ethers

Parent Compound	Position of Substituents										M.P., °C.	Refer- ences
	2	3	4	5	6	2'	3'	4'	5'	6'		
	OH	OH	119-120 122-123 123-124 120-121 123-124	53 78 98 103 147
	OH	CH ₃	OH	CH ₃	101-102	73
	OH	CH ₃	CH ₃	OH	CH ₃	CH ₃	99-100 100-101 98-99	99 99 99
	CH ₃	OH	CH ₃	CH ₃	OH	CH ₃	171-172.5	44
	OH	CH ₃	cyclo-C ₆ H ₁₁	OH	CH ₃	cyclo-C ₆ H ₁₁	145	199
	OH	cyclo-C ₆ H ₁₁	CH ₃	OH	cyclo-C ₆ H ₁₁	CH ₃	169	101
	OH	Cl	Cl	OH	Cl	Cl	110-111 110-111	102 103
	OH	Br	CH ₃	OH	Br	CH ₃	75.5-76.5	104
	Br	CH ₃	OH	CH ₃	Br	Br	CH ₃	OH	CH ₃	Br	252	79

tures slightly above the melting point of the phenol alcohol. At higher temperatures formaldehyde was lost and methylene bridge formation and other reactions set in. This sequence of reaction apparently is not always followed, according to Adler,⁵⁸ who made a thorough study of the products formed on heating 2,6-dimethyl-4-methylolphenol at various temperatures. At 140°C. the loss of formaldehyde and the formation of methylene derivatives were the most important reactions. At 155°C. the dibenzyl ether was formed in greatest quantity. However, when the temperature was raised to 170–180°C., neither the methylene nor the dibenzyl ethers were formed, but instead a mixture of dihydroxydiphenylethane and dihydroxydiphenylethylene was found. These and other results serve to illustrate how reaction conditions as well as the structure of the phenol alcohols may influence the products obtained on heating a phenol alcohol.⁵⁷

A number of dihydroxydibenzyl ethers are listed in Table II.

Transition Products

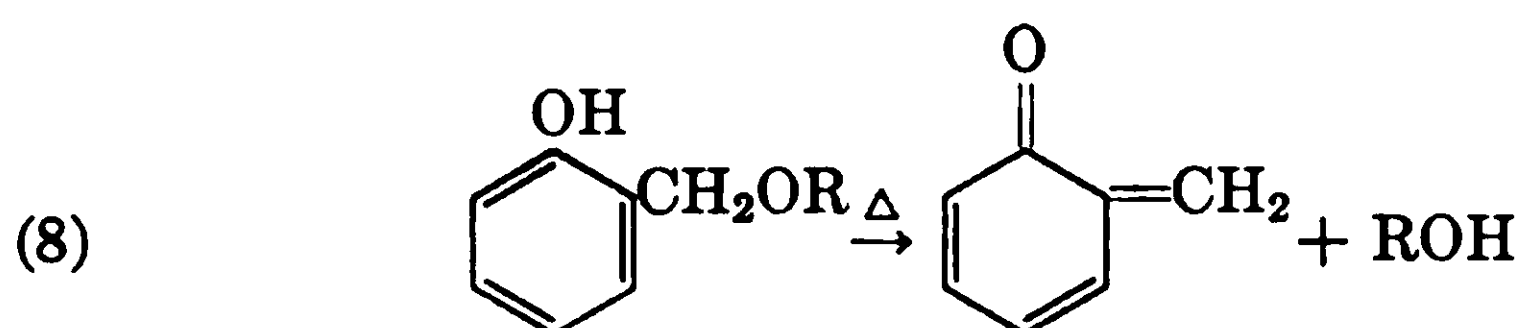
As mentioned above, the dihydroxydibenzyl ethers may function as transition and also as end products in phenolic resins. The structure of the dibenzyl ether and the reaction conditions determine whether and to what extent the ether linkage will be found in the hardened resin. Ordinarily at temperatures above about 160–170°C. the dihydroxydibenzyl ethers become unstable and undergo reactions which lead to a variety of new products. In general the products are identical with those that may be obtained by heating the parent phenol alcohol.

One of the more important transformations of a dibenzyl ether is the formation of dihydroxydiphenylmethanes. This may occur either by the loss of formaldehyde from the ether linkage or by reaction of the ether with additional phenol. The amount of formaldehyde evolved in the first reaction as well as the temperature at which the reaction sets in varies with the structure of the dibenzyl ether.^{88, 87} (See page 130.)

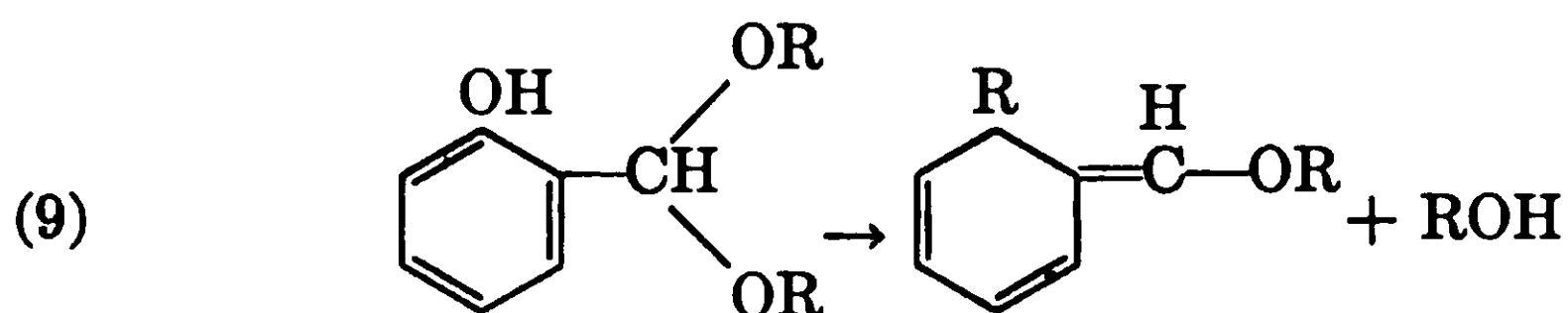
With dibenzyl ethers derived from polynuclear phenol alcohols the loss of formaldehyde is small and in certain cases is barely detectable,^{88, 87–89, 105–109} whereas water may be evolved in large amounts. Although dibenzyl ethers are readily formed from phenol alcohols in which the phenolic hydroxyl group has been blocked by esterification or etherification, formaldehyde is lost only from the ethers possessing a free phenolic hydroxyl group.^{74, 82, 88, 105} The loss of formaldehyde

from a dihydroxydibenzyl ether may occur under neutral conditions but is accelerated by alkalies and by acids.^{78, 98, 88}

Any explanation of the loss of formaldehyde from a dibenzyl ether should also explain why less than a mole of formaldehyde is evolved per mole of ether. It should also take into account the fact that a free phenolic hydroxyl group is required for the reaction. In their early papers Zinke and Hanus¹⁰⁸ suggested that part of the formaldehyde evolved might recombine with a reactive position in the resins, possibly at a methylene bridge. Zinke and his coworkers^{41, 82, 108} also found aldehyde and methyl-substituted phenols among the decomposition products of dibenzyl ethers. This suggested that the deficiency of formaldehyde evolved might be traced to side reactions which consumed the ether in other ways. On the other hand, Hultzsche^{4, 87} and Euler⁴⁴ think that the dibenzyl ethers may split at high temperatures to a phenol alcohol and a quinone methide. The regenerated phenol alcohol may either lose formaldehyde at the elevated temperature or dehydrate to a new quinone methide. If formaldehyde is lost the free phenol obtained may then react with the quinone methide in the system to form a dihydroxydiphenylmethane. On the other hand, if the phenol alcohol dehydrates to a quinone methide then any of the complex oxidation-reduction or polymerization products of the quinone methides might result. This mechanism explains most, if not all, of the experimental findings. A further argument for this mechanism may be found in the work of Thiele and Dimroth,¹¹⁰ who found that the methyl and ethyl ethers of saligenin decomposed to a brown resin and alcohol on heating, reaction 8.



A similar reaction occurs on heating salicylaldehyde acetal,¹¹¹ reaction 9.



The formation of a dihydroxydiphenylmethane by reaction of a phenol with a dihydroxydibenzyl ether is a general reaction of benzyl ethers and does not depend on the presence of a phenolic hydroxyl

group on the benzene ring. The same product is obtained by reaction of either a dihydroxydibenzyl ether or the parent phenol alcohol with the phenol. The dibenzyl ether actually may be an intermediate in the reaction of a benzyl alcohol with an aromatic compound such as phenol.¹¹² Although dihydroxydibenzyl ethers will react with phenols at high temperatures under neutral conditions the reaction proceeds most readily under acidic conditions. In those instances where the dibenzyl ether is devoid of an activating group such as that provided by the phenolic hydroxyl group the reaction proceeds poorly, if at all, under neutral conditions.

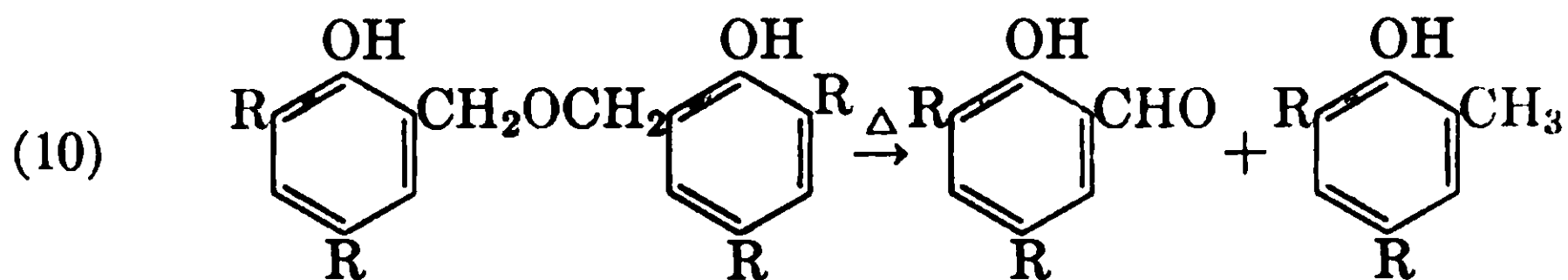
In the reaction of benzyl alcohol with phenol, Zalkinol and Kurlina¹¹⁸ have reported the formation of phenylbenzyl ether. This might suggest that reaction of a phenol alcohol or dibenzyl ether with phenols occurs first at the phenolic hydroxyl group followed by rearrangement onto the ring. Phenylbenzyl ethers in phenolic resins were suggested by Baekeland^{18,18} as early as 1909.

Phenol Aldehydes and Methyl-Substituted Phenols

Phenol aldehydes are found among the products formed by heating dibenzyl ethers or their precursors, the phenol alcohols, at elevated temperatures. Ordinarily such products are formed in small amounts, but certain isolated compounds give fair yields of aldehydes.^{108,114} For example, Zinke and Ziegler¹⁰⁸ obtained 0.8 gram of 3,5-dichloro-2-hydroxybenzaldehyde from 2.7 grams bis(3,5-dichloro-2-hydroxybenzyl) ether. Both mono- and dialdehydes have been detected among the products obtained on heating dihydroxydibenzyl ethers.^{44,78,82,100,105,106,114,115}

Quinone methides have been suggested as the active intermediates for the formation of aldehydes from dibenzyl ethers, and small amounts of aldehydes have been obtained by Hultsch by heating certain polymeric quinone methides.^{4,89,94,100,118} However, Zinke and Ziegler⁹⁷ were unable to obtain aldehydes on decomposing 3,5-dichloroquinone-2-methide or the 3,5-dimethylquinone-2-methide. They showed further that dibenzyl ethers and phenol alcohols with blocked phenolic hydroxyl groups also yield methyl and aldehyde derivatives on heating at high temperatures.^{41,97} Cannizzaro¹¹⁷ had found much earlier that dibenzyl ether gives toluene and benzaldehyde on thermal decomposition. In these cases a quinone methide could not be formed owing to the absence of a phenolic hydroxyl group.

Zinke⁸² believes that the aldehydes result from the cracking of dibenzyl ethers, reaction 10. This mechanism requires the formation



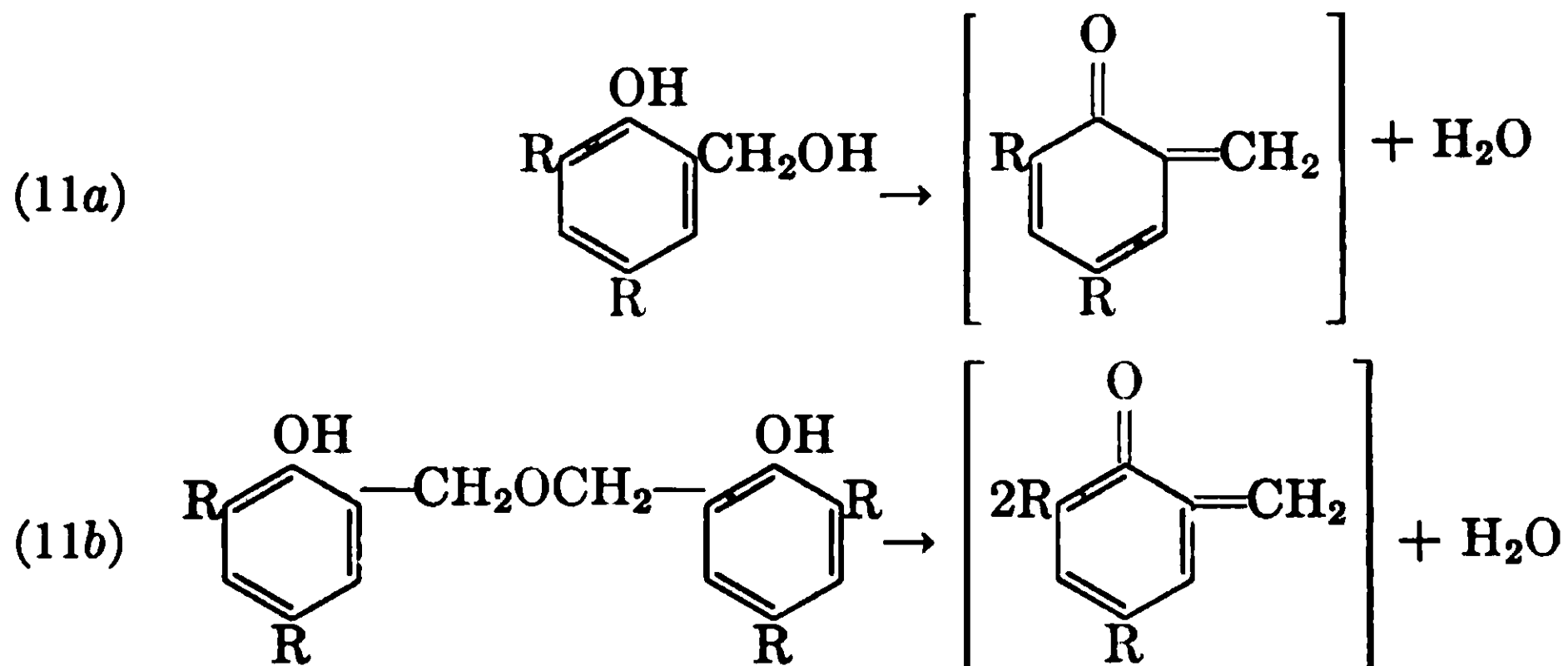
of equal molar quantities of the methyl and aldehyde derivatives. This has not been found experimentally and is one of the main arguments presented by Hultzsich against the above mechanism.¹¹⁶ Too much emphasis should not be placed on the amount of each product isolated because of the difficulties encountered in recovering the products.

Quinone Methides

The quinone methides constitute an exceedingly reactive and interesting group of products obtained by heating dihydroxydibenzyl ethers or phenol alcohols above their decomposition point. It has also been suggested that quinone methides may result by splitting phenol from the end of a novolac resin chain.^{40, 98} Such compounds were first suggested as intermediates in the cure of phenolic resins by Wohl and Mylo,¹¹⁸ although Baekeland²¹ and Novak and Cech¹¹⁹ thought that polymerization as well as condensation reactions were involved in the cure of phenolic resins. Though not concerned with phenolic resins, a discussion of the chemistry of quinone methides would not be complete without referring to the work of Auwers,^{78, 120-128} Zincke,^{68, 124} as well as that of Fries and coworkers.¹²⁵⁻¹²⁷ Hultzsich,^{87, 89, 100, 106, 128-132} Euler,^{44, 57, 78, 133-134} and Adler^{56, 104} have actively sought to clarify the role of the quinone methides in phenol-aldehyde chemistry. Hultzsich takes the view that they are the active intermediates in essentially all reactions of phenols with aldehydes. In his 1950 book⁴ he has given a detailed discussion of the active form of the intermediate and the arguments for his position. Though convinced of the importance of quinone methides, Euler and coworkers⁴⁴ have assigned a lesser role to the materials and hold to the view that they are involved mainly in the reactions at high temperatures. Once formed they may function as active intermediates for reaction with other materials in the system or they may polymerize. The position taken by Euler seems best supported by the experimental data.

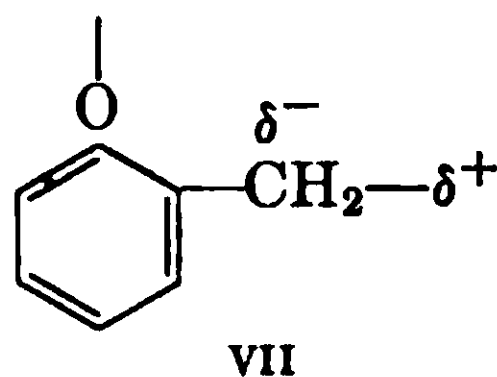
Although the dimeric and trimeric forms of the quinone methides have been isolated, the monomeric materials cannot be obtained on account of their extreme reactivity. Treatment of halomethylphenols in an inert solvent with a dilute aqueous solution of alkali provides the simplest means for obtaining the dimeric and trimeric materials.¹²⁸

Oxidation of methyl-substituted phenols has also been used.¹⁸⁵ Identical products can be formed, but in lower yield, by heating the corresponding phenol alcohols or dibenzyl ethers at temperatures ranging from 170° to over 200°C., reactions 11a and 11b. Both reactions

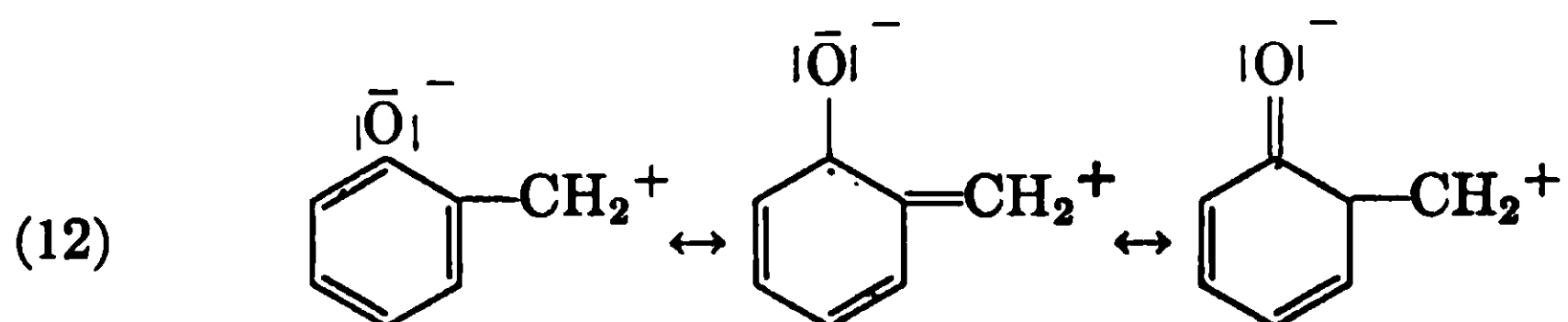


probably occur simultaneously on heating a phenol alcohol to around 200°C., part of the alcohol going directly to the quinone methide, and part first being converted to the dibenzyl ether which then forms the quinone methide. One of the strongest arguments for reactions 11 has been the measurement of the water evolved during the heating of phenol alcohols or dibenzyl ethers.^{88, 74, 95, 107} In certain instances as much as 1.85 moles of water per mole of *p*-substituted phenol dialcohol has been obtained.⁸⁸

Since quinone methides possess a carbonyl group conjugated with a terminal methylene group a high degree of reactivity would be anticipated. Their reactivity apparently exceeds that of the vinyl ketones, which also have such a structure. To explain the extreme reactivity of the compounds better, electronic structures also have been suggested. Lilley¹³⁶ has pictured the active form of the quinone methide as shown in VII; Hultzs⁴ prefers a "Zwitterion" with the following



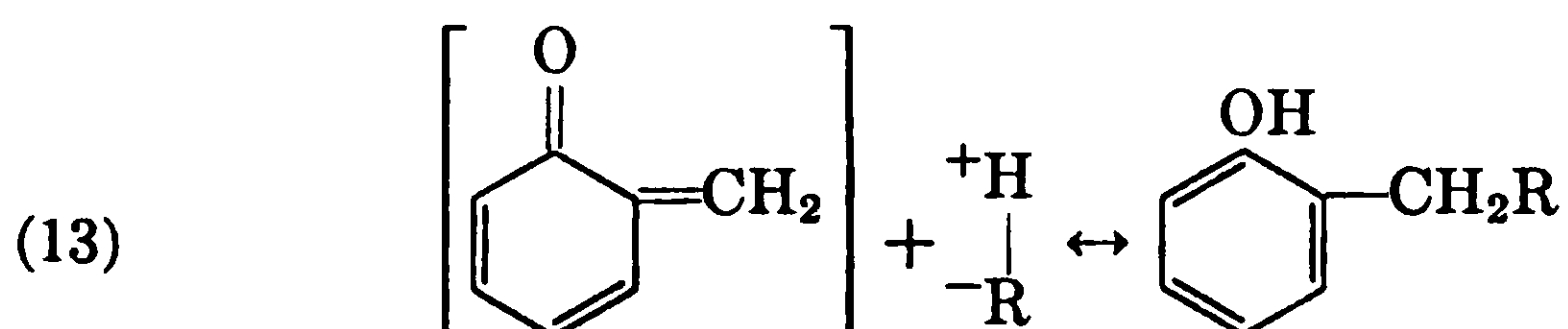
limiting formulas; equation 12.



The reactions of quinone methides have been classified into four groups: ¹²⁹

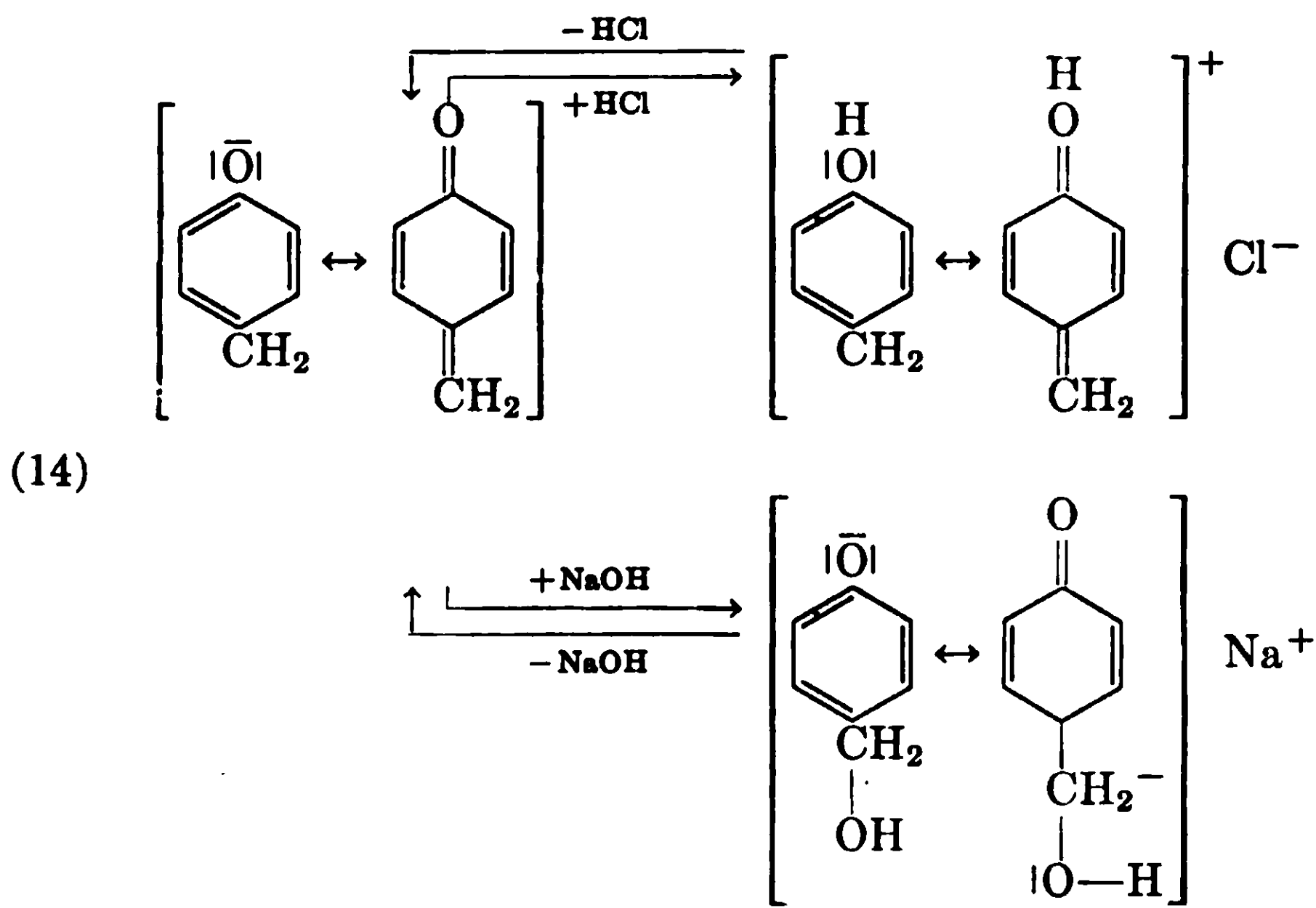
1. Addition of compounds with acidic hydrogen.
2. Oxidation-reduction reactions.
3. Addition of unsaturated compounds.
4. Polymerization reactions.

The first type of reaction can be represented by the general equation, reaction 13. Hultzscher contends that all common reactions such



as the formation of phenol alcohols, dibenzyl ether, dihydroxydiphenylmethanes, and hydroxybenzylamines occur by addition of the proper materials with acidic hydrogens (water, phenol alcohol, phenol, and an amine) to a quinone methide.

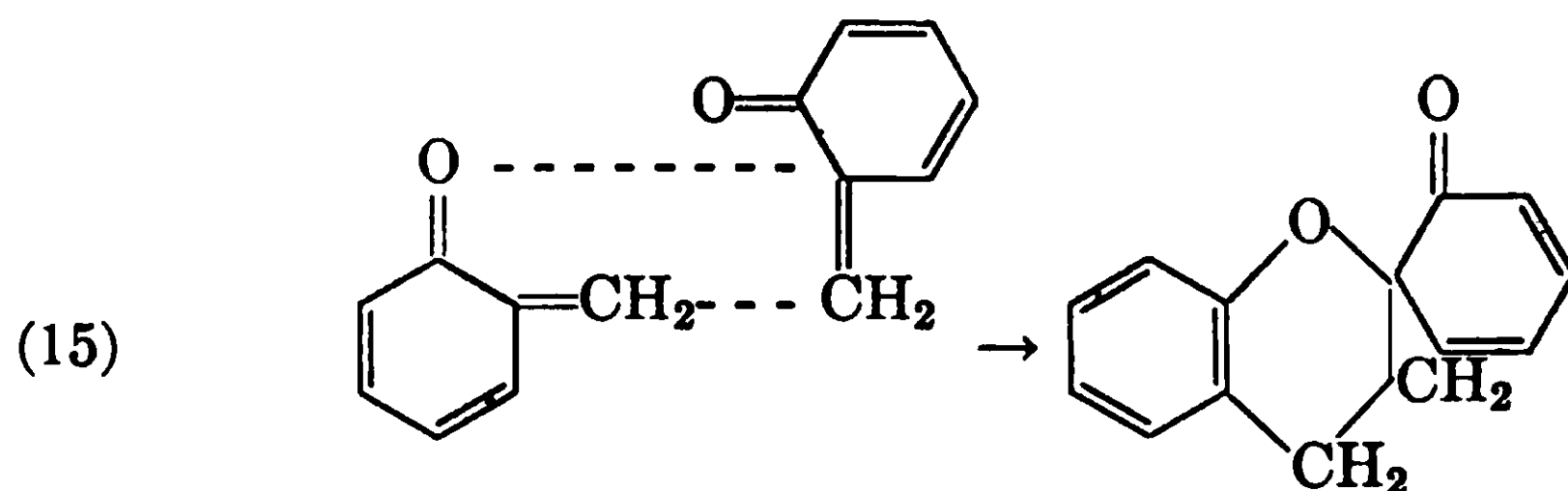
Closely associated with the addition of compounds possessing acidic hydrogens is the possibility of salt formation, equations 14. This



mechanism has been employed to explain the acid and base catalysis of reactions presumed to involve quinone methides.

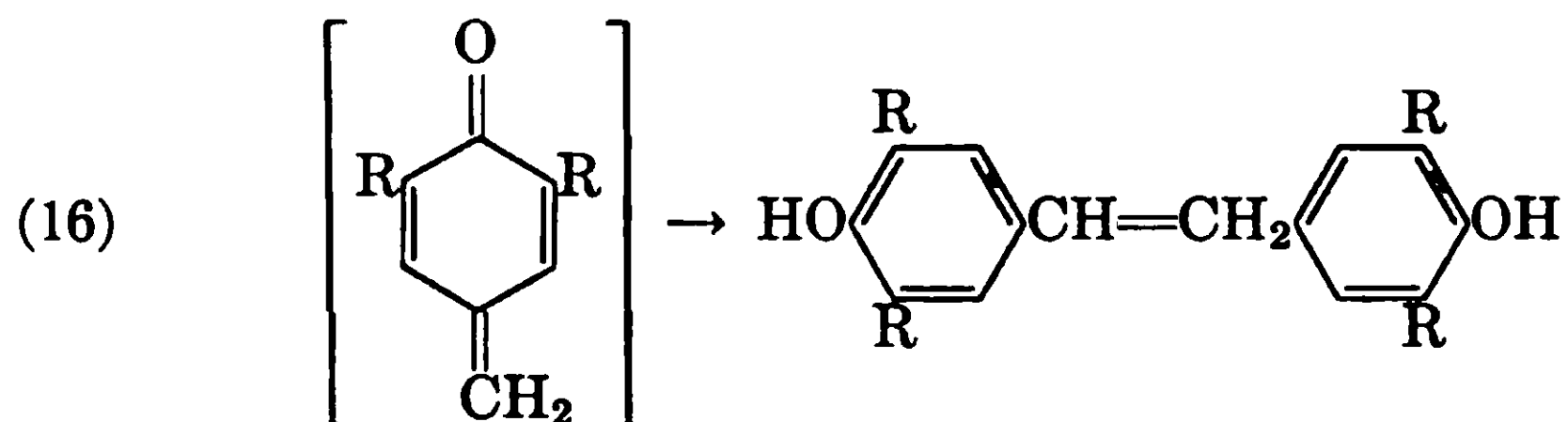
The addition of quinone methides to unsaturates will be discussed in Chapter 8.

The *ortho* and *para* quinone methides give different products on polymerization. The *ortho* quinone methides give cyclic ethers,^{89, 135, 129, 132} equation 15. In the formation of these compounds the quinone

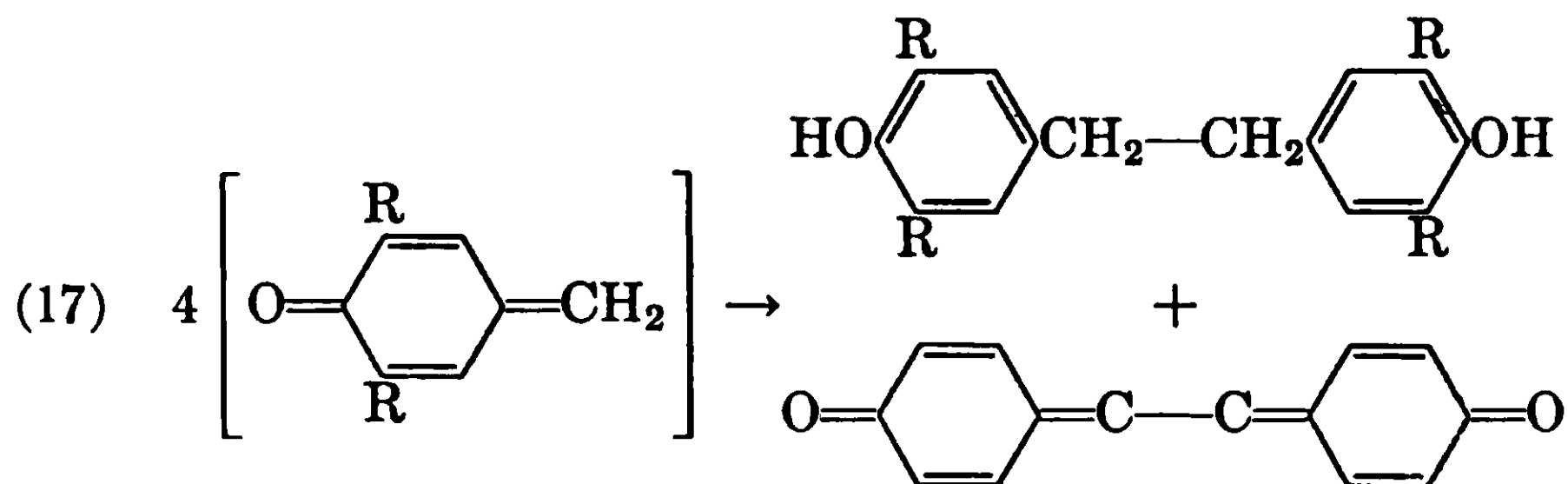


methide functions both as the diene and as the dieneophile in a Diels-Alder reaction. The product represents one of a few examples where a spiro carbon is formed in a Diels-Alder reaction.

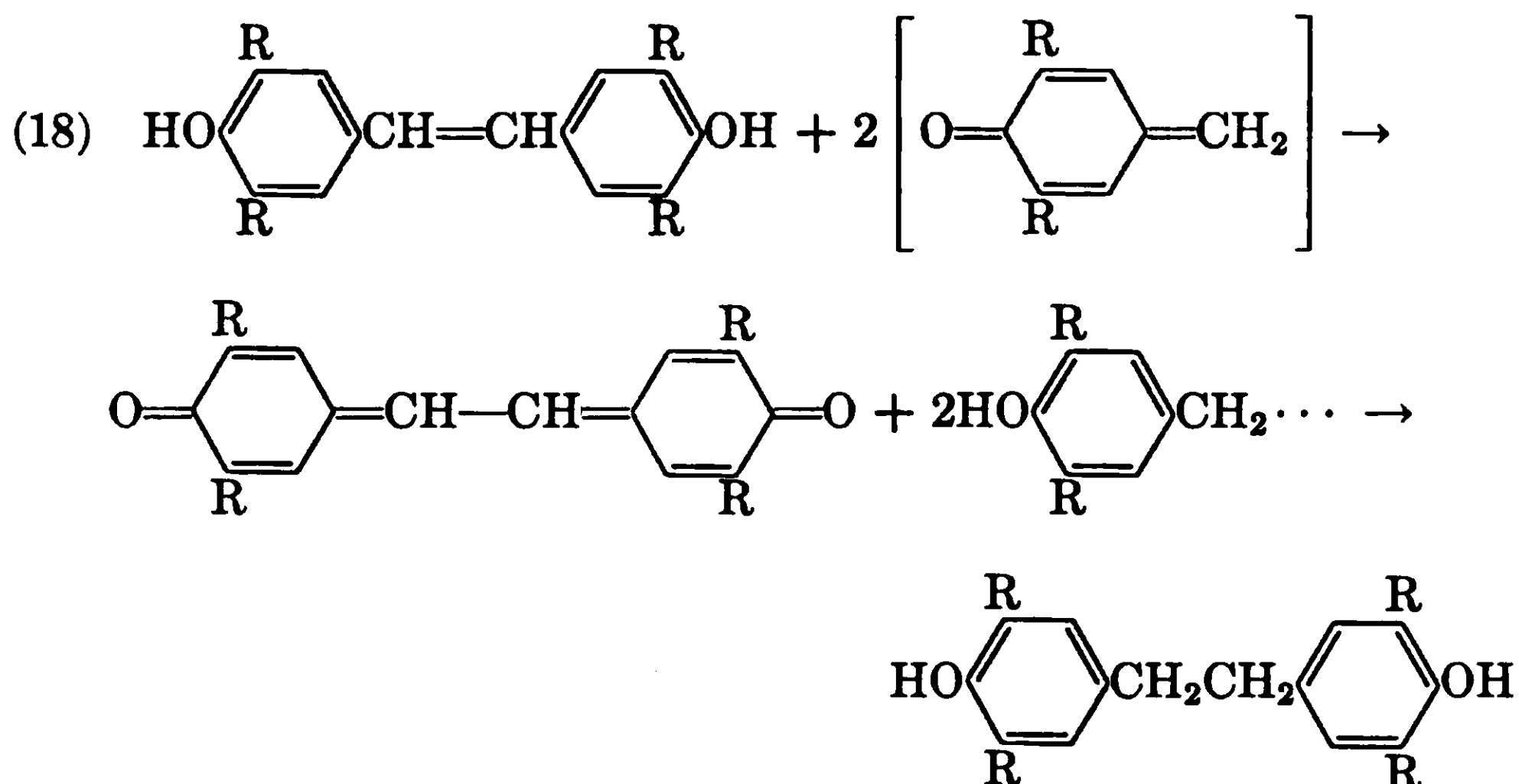
The *para* quinone methides on dimerization give dihydroxystilbenes, reaction 16. According to Euler, Adler, and Caspersson¹³⁴ this is the only polymerization reaction of the *p*-quinone methides.



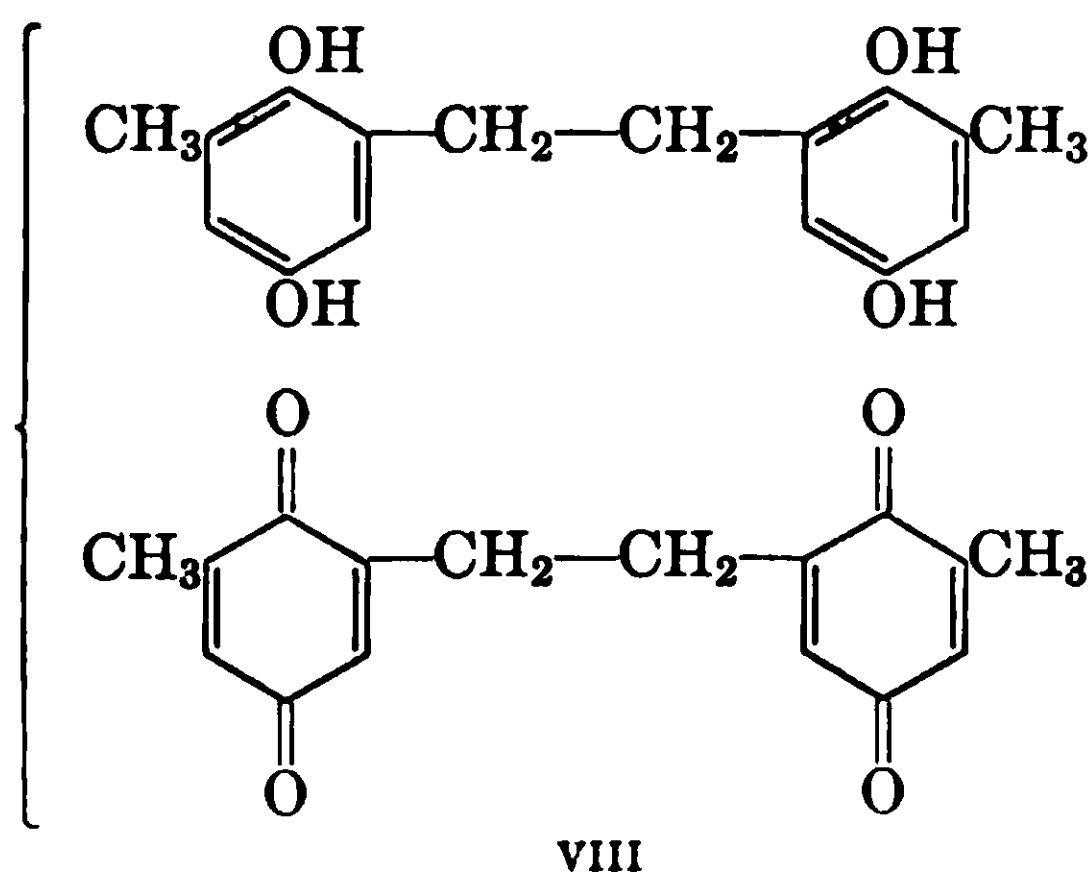
The quinone methides may also undergo a disproportionation reaction in which a stilbene-quinone and a dihydroxydiphenylethane are formed,^{53, 104} reaction 17. This type of reaction may be viewed as



one of the many oxidation-reduction reactions of the quinone methides. These reactions have been studied in detail by Euler and Adler and their coworkers.^{44, 56, 57, 73, 133} Euler, Adler, and Caspersson¹³⁴ have pictured the reaction as proceeding as in equation 18.

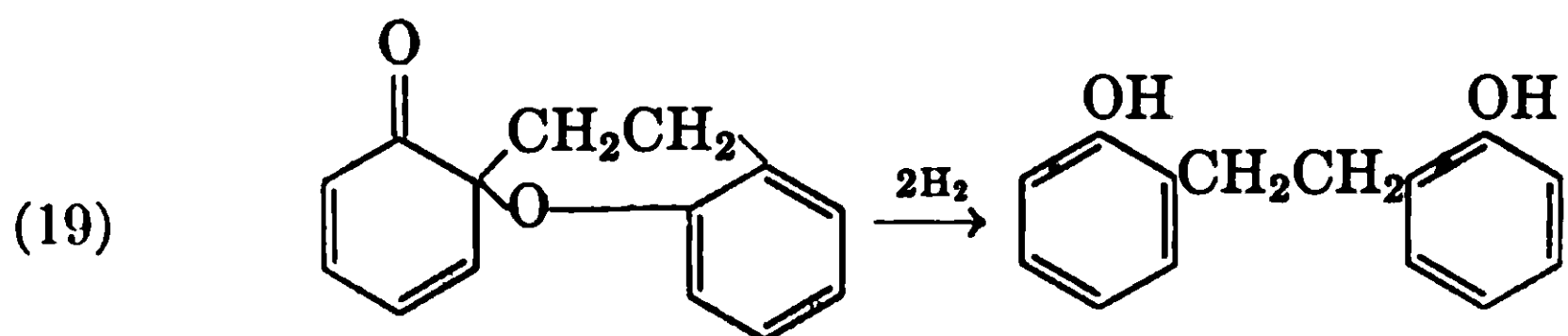


Some interesting results were obtained with the monoalcohol of toluhydroquinone.¹³⁴ The ethane and quinone derivatives were prepared independently. When they were mixed, an intensely violet-colored quinhydrone, VIII, was formed. Similar quinhydrone com-

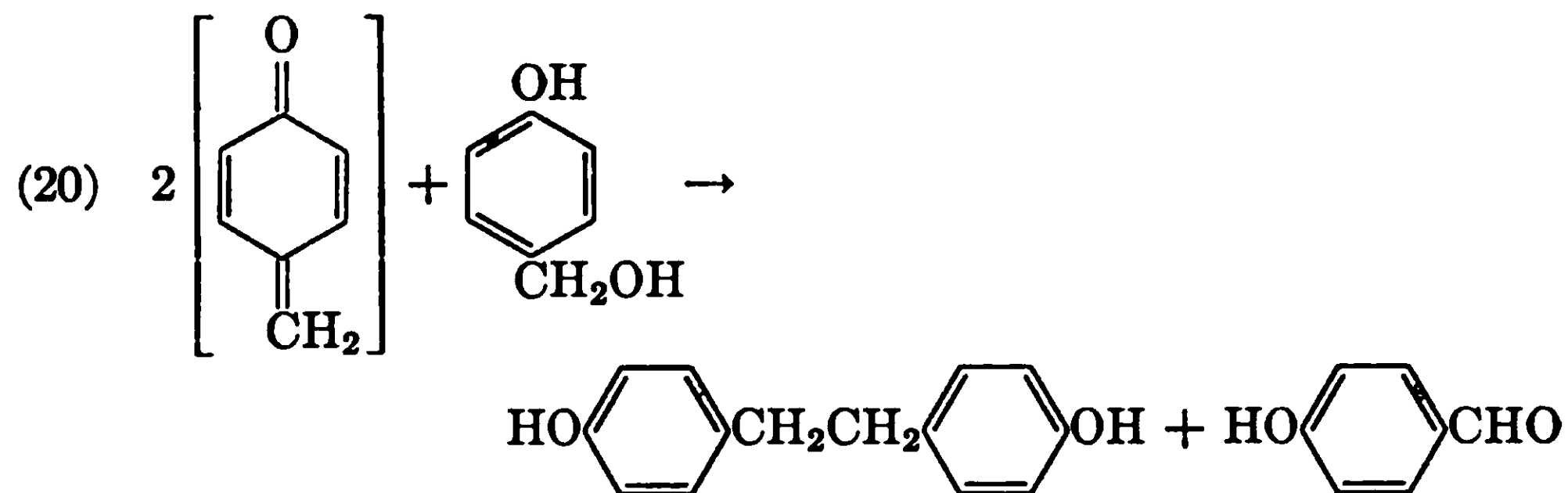


plexes may be in part responsible for the color of phenolic resins cured at high temperatures.

Another mechanism suggested for the formation of the di-(*o*-hydroxyphenyl)ethanes is by reduction of the cyclic ethers,⁴⁴ reaction 19.

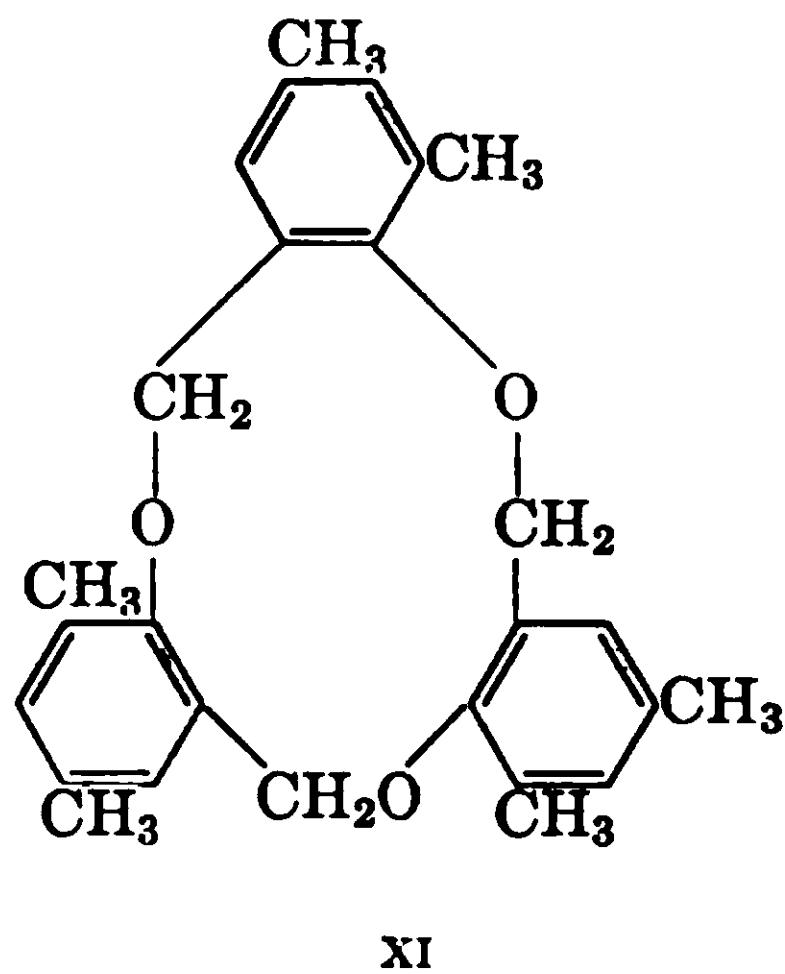
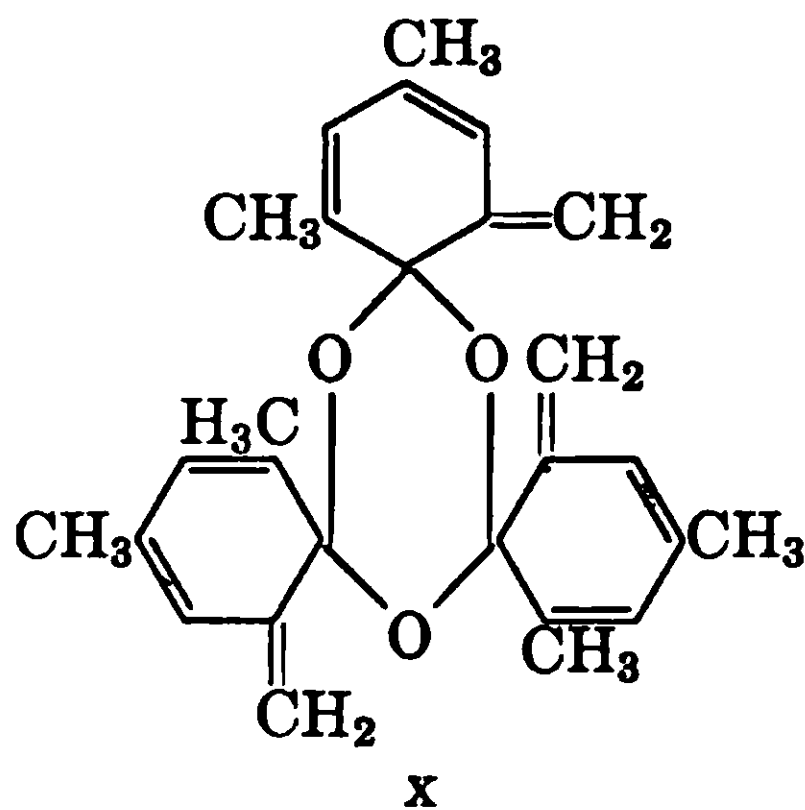
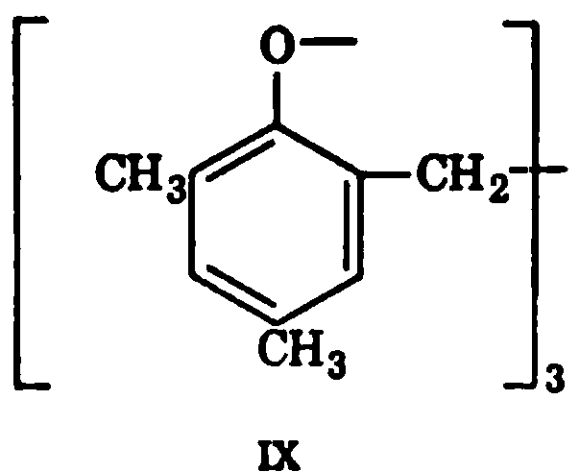


The formation of di(hydroxyphenyl)ethanes by still a third mechanism has been considered. This mechanism involves the reaction of 1 mole of a phenol alcohol with 2 moles of a quinone methide.² A phenol aldehyde would be a by-product of this reaction, reaction 20.



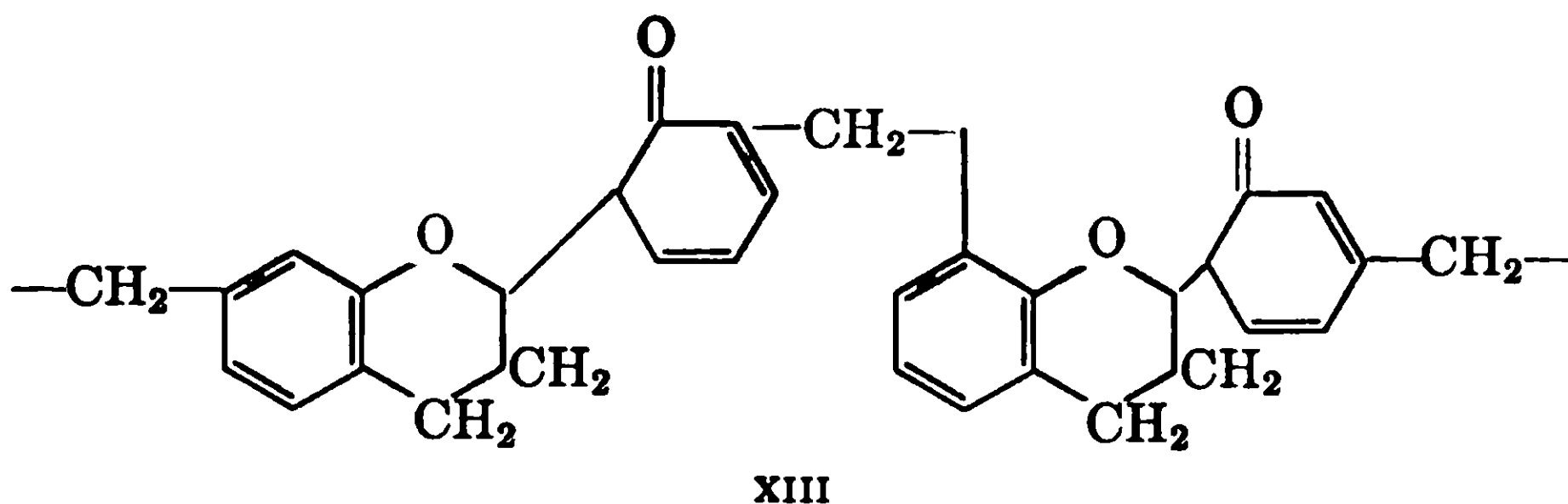
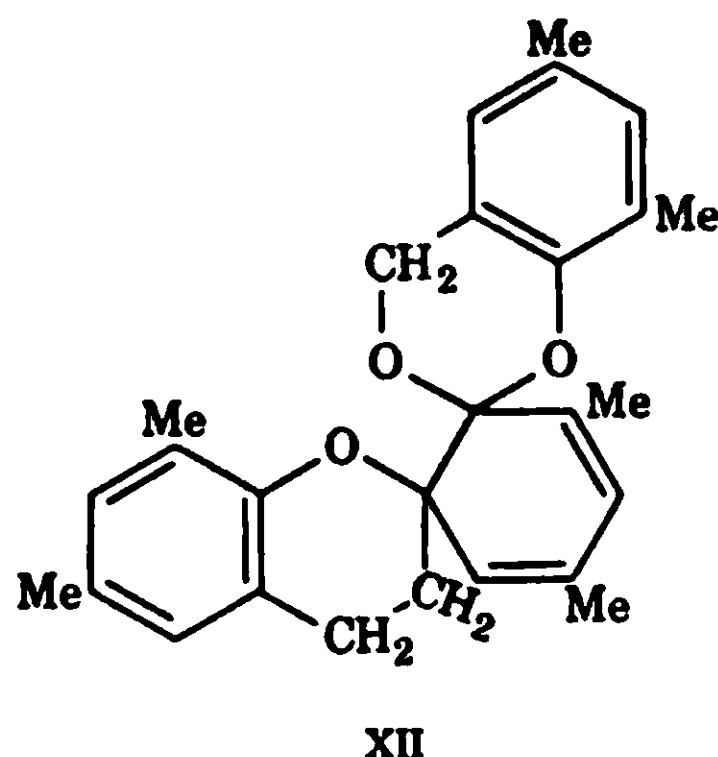
This reaction has not been proved experimentally.

The final reaction of quinone methides, excluding the reaction with unsaturates which will be considered in Chapter 8, is the formation of polymers. The structure of these compounds has received considerable attention. 2,4-Dimethyl-6-methylolphenol forms a quinone methide on heating. According to Euler, Adler, and Caspersson,¹³⁴ the quinone methide may undergo three reactions. It may dimerize to a yellow quinol ether, already discussed; it may undergo internal oxidation-reduction reactions, also discussed above; or it may form a colorless trimer. Since the trimer was colorless and the structure was not entirely clear these authors represented the compound as IX. In a somewhat earlier publication the two structures X and XI were rejected by Euler, Adler,

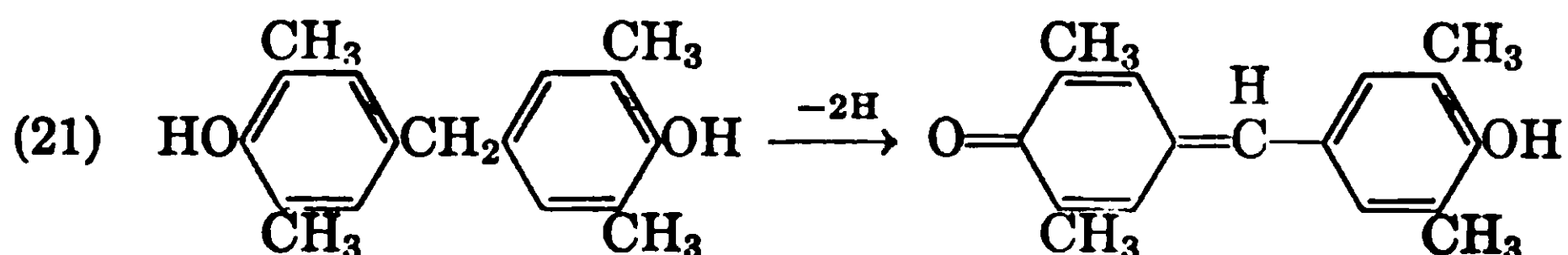


and Cedwall.⁵⁷ Schiemann and Hultzs¹⁸⁷ have studied the same quinone methide and have formulated its structure as shown in XII. This structure is a combination of the known dimeric cyclic quinone ether and the benzodioxans. According to Schiemann and Hultzs, the various properties of the trimer, including its lack of color and its decomposition at 200°C. to give mesitol and dihydroxybimesityl and the products obtained on acetylation,¹²⁶ are all explained by the structure given above.

Polymers higher than the trimer are also formed under certain conditions. On heating 3,5-dimethyl-2-hydroxybenzyl alcohol to 170–200° for a short time, Hultzs⁵⁷ obtained the dimeric or trimeric o-quinone methides. These methides resinified further on heating to about 220°C., and a black product was formed without loss of water or formaldehyde. Distillation of the reaction product yielded bis(3,5-dimethyl-2-hydroxyphenyl)ethane and a dark brown resin with a molecular weight of 500–650, pointing to 4–6 ring members. In the formation of such products oxidation-reduction reactions play an important part. Chains, involving both cyclic quinone ethers and methylene bridges, XIII, have been proposed to explain the molecular weights obtained.¹⁰⁶



Fries and Brandes¹²⁸ as well as Euler, Adler, Cedwall, and Torn-gren⁴⁴ have obtained small quantities of a *p*-hydroxyphenylmethylene quinone from dihydroxydiphenylmethanes. These compounds appear to have been formed by oxidation of a dihydroxydiphenylmethane rather than from a quinone methide as might be expected, reaction 21.



It has been suggested that these compounds are responsible for much of the discoloration of phenolic resins caused by oxidation.

Summary

In the purely thermal hardening of phenol alcohols or One-Stage resins, the formation of dibenzyl ethers is a very important reaction with the substituted phenols if the hardening temperature is held below about 160°C. The reaction also occurs but assumes somewhat less importance if the resins are derived from trifunctional phenols. If the system is alkaline, methylene derivatives appear to be formed exclusively. Under acidic conditions both dibenzyl ether and methylene linkages may be formed, but if the conditions are strongly acidic the methylene derivative will be the major if not the exclusive product.

The dibenzyl ethers are unstable at high temperatures and may undergo further reactions. The methylene bridge, on the other hand, is a very stable linkage and normally it is not destroyed below the point of complete decomposition of the resin. Since conditions are seldom neutral the methylene bridge is probably the most common linkage found in a cured One-Stage resin derived from a trifunctional phenol.

At temperatures between 160° or 170°C. and 250°C., second phase of condensation, many complex changes may occur in a resin. The molecular weight first increases and then declines. During this period the number of dibenzyl ether linkages decreases rapidly while the number of methylene bridges usually increases. Small quantities of methyl and aldehyde phenols may be eliminated as volatile products. Simultaneously reactions involving the formation of quinone methides and their polymerization and oxidation-reduction products occur. These reactions lead to extremely complex products which are at best only poorly understood.

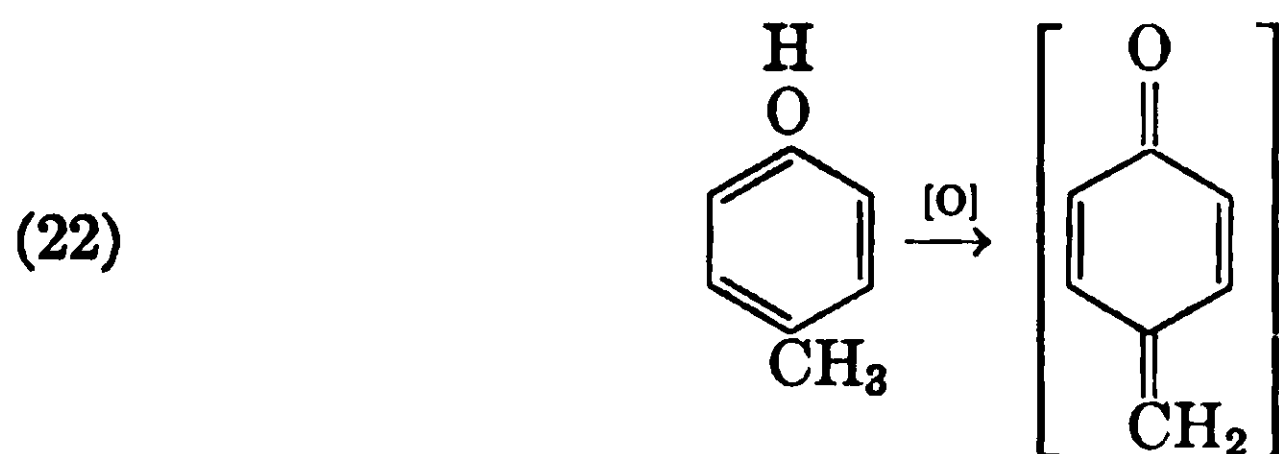
Sources of Added Functionality for Cure of Phenol Alcohols and One-Stage Resins

A curing resin should be obtained only from those phenols having more than two reactive *ortho* or *para* hydrogens. Likewise linear polymers should result when the phenol has two reactive hydrogens, and a dihydroxydiphenylmethane should be the only product when a monofunctional phenol is reacted with formaldehyde. However, it has been observed^{5-7, 133, 139} that many difunctional phenols will form insoluble and infusible products and certain monofunctional phenols

will form resins in place of dihydroxydiphenylmethanes when treated with formaldehyde. Ordinarily vigorous conditions are required to bring about such reactions, but with certain phenols relatively mild conditions are adequate. For example, 4-chlororesorcinol and methylphloroglucinol give insoluble, infusible resins even at room temperature when reacted with formaldehyde. The source of the added functionality above that supplied by the reactive *ortho* and *para* ring hydrogens has been considered by many workers. As yet complete agreement on the subject does not exist, probably because a single explanation cannot be given for this puzzling phenomenon.

One of the most common suggestions as to the origin of the increased functionality is the formation of quinone methides. As already shown, quinone methides are capable of forming linear and cyclic dimers as well as cyclic trimers and higher polymers. If a quinone methide was generated only at one end of a resin molecule extensive branching would be expected. However, if an occasional quinone methide was formed at both ends of a resin molecule true cross linking could result even with resins prepared from *ortho*- or *para*-substituted phenols. The intense discoloration which accompanies the cure of resins derived from *ortho*- or *para*-substituted phenols is consistent with the unsaturated nature of the quinone methides and their oxidation-reduction products. Resinification through quinone methides would result in a decrease in the phenolic hydroxyl content of the resin, a fact which also has been observed experimentally.¹⁴⁰

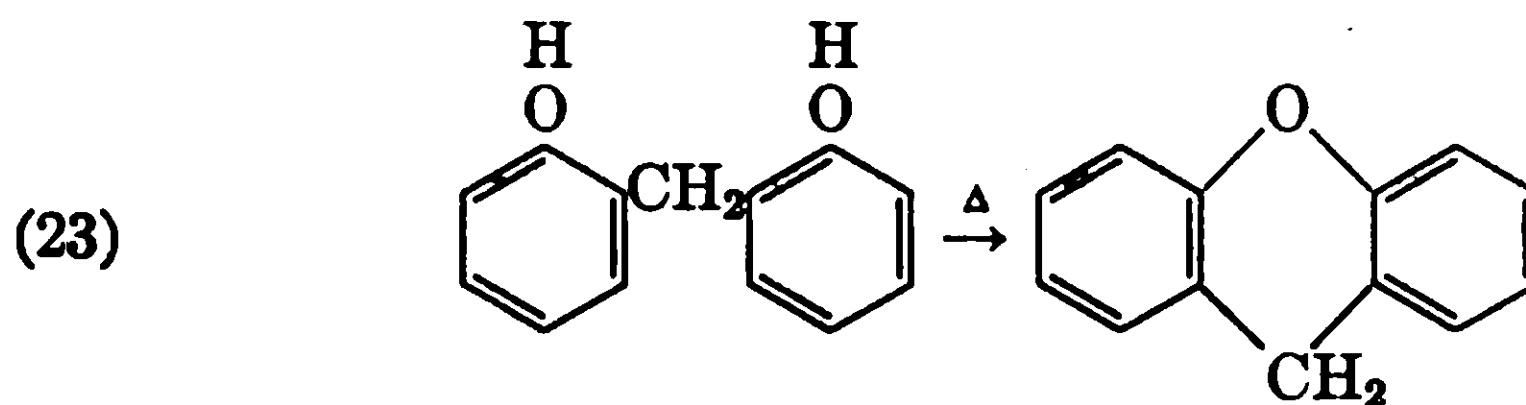
It has been suggested that phenols with *para*-methyl groups also may become involved in the formation of quinone methides by oxidative processes,⁴ reaction 22. Pummerer^{184,141} has obtained quinone



methides, or diradicals as he prefers to call them, by the oxidation of tetrachloro-*p*-cresol.

A decrease in the phenolic hydroxyl content of a resin as well as the formation of more than a mole of water from a phenol dialcohol could also be explained by condensation through the phenolic groups. An intramolecular reaction of this type occurs on heating 2,2'-dihy-

droxydiphenylmethane to high temperatures, reaction 23. Megson ³¹

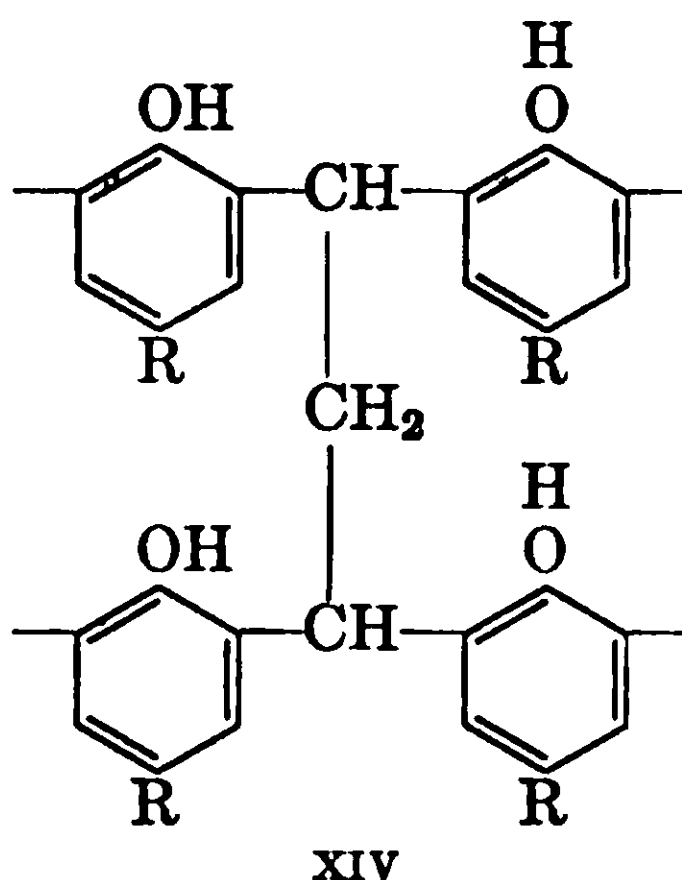


has isolated xanthene and various homologs of xanthene from the products obtained by pyrolysis of phenolic resins. The reaction might occur to a minor extent during the very high-temperature cure of a resin. However, it would not increase the molecular weight or lead to cross linking of the resin unless the loss of water occurred between the phenolic hydroxyl groups of separate polymer molecules. To date, proof of an intermolecular condensation of this type is lacking.

Thus far, it has been assumed that only the *ortho* and *para* positions of a phenol are reactive. Megson ^{6,7,30} has argued that the *meta* positions may also become reactive, and Finn, Megson, and Whittaker ¹⁴² have prepared methylene and methylol derivatives of mesitol which has no free *ortho* or *para* positions. Martin ¹⁴³ also has found that reaction occurs at the *meta* position during the condensation of certain *para*-substituted 2,6-dimethylolanisoles. Nickerson ¹⁴⁴ and Lilley ³ also think that reaction at the *meta* position should not be ruled out, particularly with compounds like *p*-cresol where the methyl groups might activate the *meta* positions. Imoto ¹⁴⁵ has discussed the hyperconjugation effect of the methyl group in compounds such as mesitol and 2,4-xylenol as related to resinification with these phenols.

Owing to the strong *ortho-para* directing effects of the phenolic hydroxyl group, it appears that reaction at the *meta* position would occur only to a minor extent, if at all, as long as free *ortho* and *para* positions were available for reaction. As the condensation reactions proceed, the available *ortho* and *para* positions may be consumed before all the methylol or dibenzyl ethers have reacted. This would be likely to occur in resins prepared with a high ratio of formaldehyde to phenol. Under these conditions, particularly in the presence of acidic reagents, condensation at the *meta* position would be more likely. However, reaction at the *meta* position would not explain the cure of resins from phenols such as methylphloroglucinol and hemimellitenol which have only two free positions on the phenol ring both of which are *ortho* to the phenolic hydroxyl groups. In these instances the formation of quinone methides or reaction at a methyl group might be considered.

A reaction occasionally suggested for resins high in methylol content, such as the casting resins, is condensation of formaldehyde, split off during heating, with a methylene bridge. Zinke and Hanus¹⁰⁸ at one time presented data and theoretical arguments for such a reaction. Their main argument centered around the observation that certain phenol alcohols, particularly the polynuclear alcohols, evolve less than a mole of formaldehyde but split off well over a mole of water on heating. It was suggested that part of the excess water resulted from the condensation of the methylene bridges with formaldehyde split off during resinification. The reaction would result in structures such as XIV and would represent one means for increasing the functionality of a resin. However, unequivocal proof for the reaction has not been obtained. The loss of more than a mole of water and less than a mole of formaldehyde on heating of *p*-substi-



tuted phenol dialcohols may also be explained by formation of quinone methides as well as by recombination of the formaldehyde in the form of cyclic acetals.¹⁴⁸

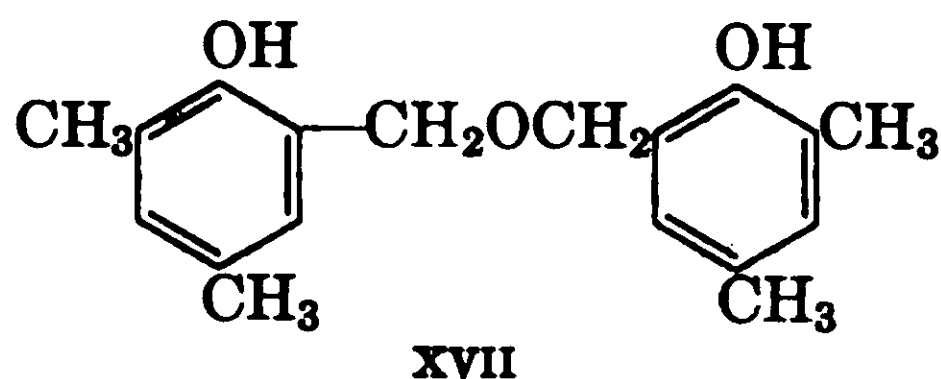
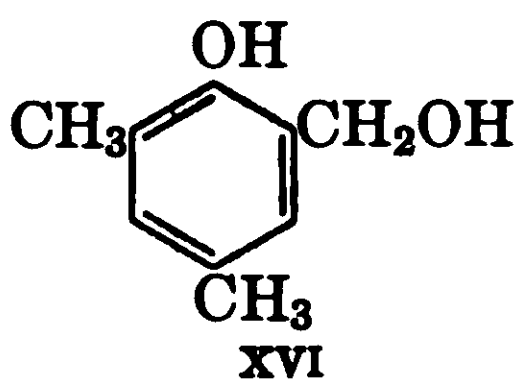
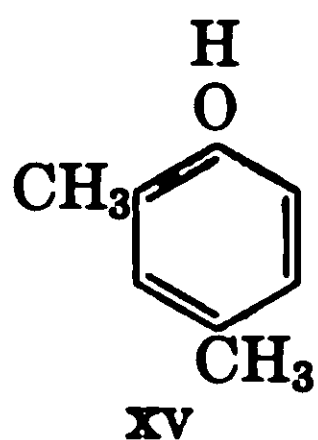
Pritchett⁹⁸ has offered a physical explanation for the "apparent" cure of resins based on difunctional phenols such as *p*-cresol. He suggests that as reaction occurs long chains are built up which form very irregular but rigid shapes. These chains may intertwine with each other and become "hooked" so that they appear to be cured; e.g., they cannot be separated by solvents or heat. Several papers have appeared dealing with the amount of rotation about a methylene or substituted methylene derivative of a phenol,^{98,142,147-149} but as yet data have not been presented to confirm Pritchett's suggestion.

B. ACID HARDENING OF ONE-STAGE RESINS

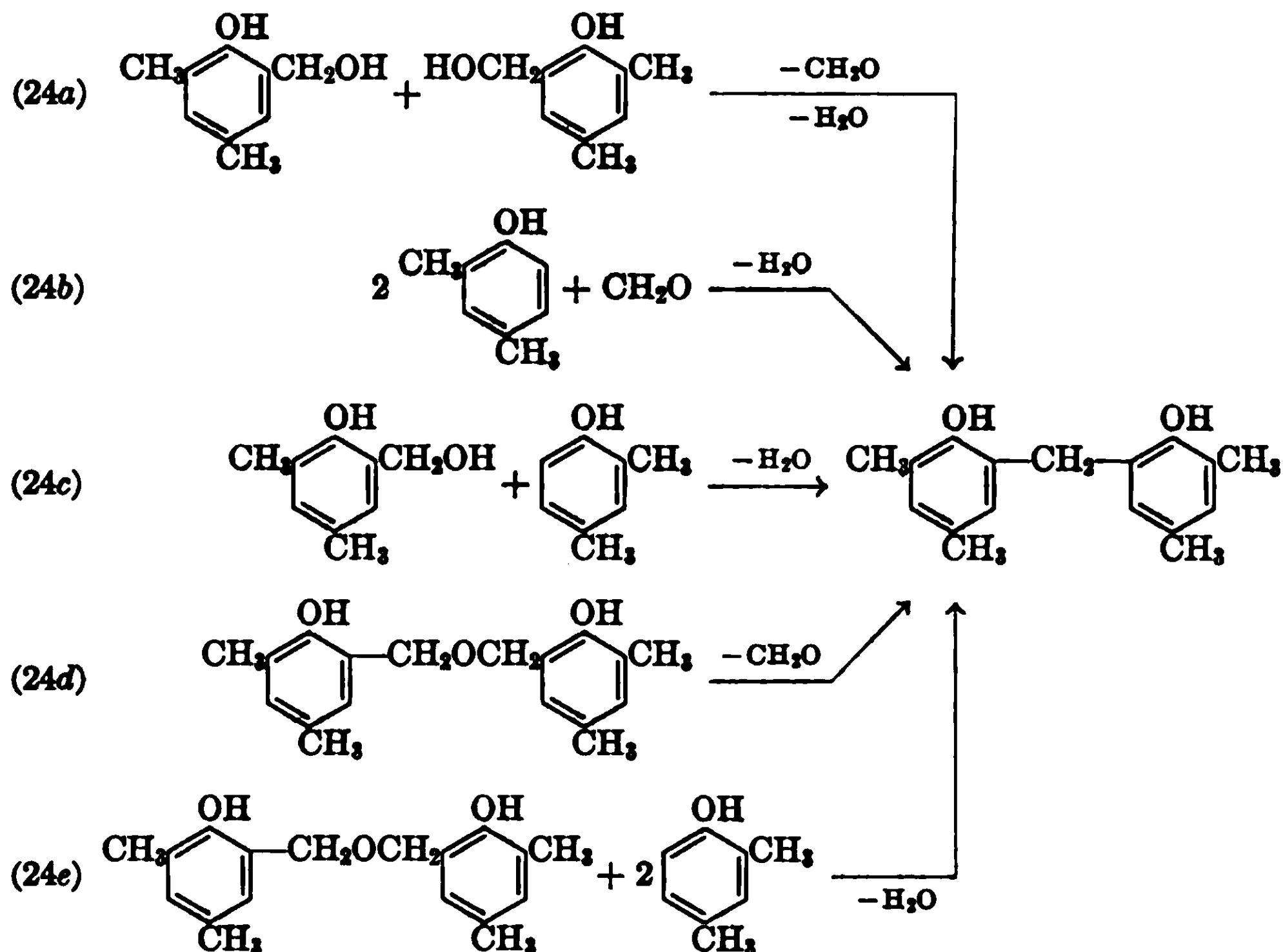
One-Stage resins, particularly those used as adhesives and casting resins, are frequently employed where cure at low or even room temperature is desirable. This is accomplished by the addition of acids, often sold under the name of a "hardener," to the resins. Acids also have been used to promote the cure of baked phenolic surface coatings. The hardeners may be prepared by dissolving acids, such as hydrochloric or phosphoric, in glycerine or glycols. *p*-Toluenesulfonic and phenolsulfonic acid as well as other sulfonic acids are also employed. The use of acids as a means for hardening phenolic resins was introduced very early.^{16,150}

A cured resin is readily obtained if phenol is reacted with an excess of formaldehyde under acidic conditions. The rate of the reaction is roughly proportional to the concentration of hydrogen ions.¹⁵¹⁻¹⁵³ As the reaction under acidic conditions is difficult to control, the formaldehyde is best combined with the phenol under alkaline conditions and the resole obtained then hardened by the addition of acid. In many respects the reactions involved are similar to those encountered in the preparation of novolac resin. The main difference is that a higher ratio of formaldehyde to phenol is employed and the formaldehyde is already chemically tied into the resin when the acid is added. As in novolac-resin formation the primary reaction in the acid hardening of a resole is the formation of methylene bridges. Where a very small quantity of acid is used as catalyst at low temperatures with a resin of high methylol content dibenzyl ethers may also be formed.^{45a}

Hultsch⁶⁰ has made a detailed study of the chemistry of acid hardening. He used compounds XV, XVI, and XVII as models for his study with toluenesulfonic acid, a common "hardener," as catalyst. The scheme shown in equations 24a to 24e indicates the reactions



found, all of which led to the same final product, namely, the dihydroxydiphenylmethane. Reese^{45a} has since found that with certain phenol alcohols the reaction may stop at the dibenzyl ether even under acidic conditions.



Each of the reactions 24a-e was carried out in a calorimeter, and the heat evolved was measured as a function of time (Fig. 4). Reaction c is by far the most exothermic of the group. This explains why the addition of a strong acid to a One-Stage resin, which almost always contains free phenol^{154,155} as well as phenol alcohols, may cause a strongly exothermic or even violent reaction.¹⁵⁶ The heat evolved

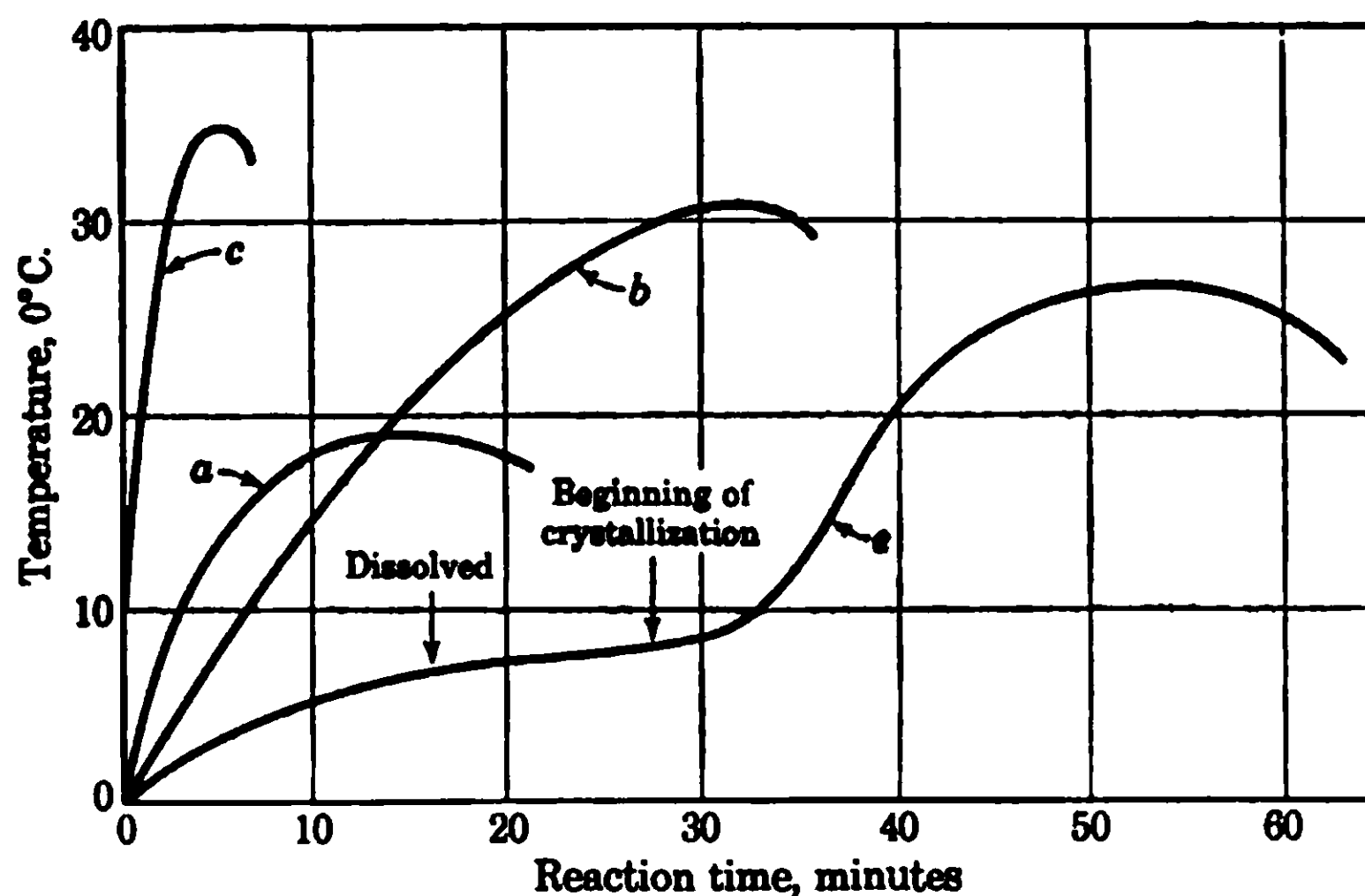


Fig. 4. Reprinted by permission of the author, K. Hultzs, from *Kunststoffe*, 37 Jahrgang, H1-12, 1947, Carl Hauser Zeitschriftenverlag, Munich.

during cure of One-Stage resins has also been measured by other workers.^{54, 157}

The highly exothermic nature of the acid-catalyzed condensation is utilized in the preparation of self-foaming phenolic resins. The heat generated by the reaction of the phenol alcohols with the free phenol, and with themselves, is sufficient to cause the formation of sufficient steam to foam the resin. The high temperature brings about cure of the resin before it collapses. Sodium bicarbonate also may be added to the resin before the addition of the acid. The reaction of the sodium bicarbonate with part of the acid may aid the foaming reaction and at the same time moderate the catalytic action of the acid.¹⁵⁵

The reaction giving off the least amount of heat is that between two phenol alcohols, reaction *a*. This fact is utilized in preparing casting resins. Besides giving better color, resoles prepared with a formaldehyde-to-phenol ratio around 2.5:1 show better storage characteristics and are more easily controlled during cure than resins made with a smaller quantity of formaldehyde.

Acid hardening occurs best at relatively low *pH* values. It is somewhat surprising to find that One-Stage phenolic resins are, in general, most stable in the *pH* range 3–5. The point of greatest stability varies somewhat with the phenol used to prepare the resin and the temperature at which cure is being effected.^{152, 155, 159, 160} Resorcinol resins are most stable at a *pH* around 3 whereas phenol resins achieve greatest stability at a *pH* closer to 4. Apparently there is a reaction catalyzed by hydrogen ions at a *pH* below 3 and by hydroxyl ions at higher *pH* values, starting at a *pH* of around 5.¹⁵⁵

Miiller and Miiller⁵⁴ have made extensive studies in the acid hardening of One-Stage resins, emphasizing the practical aspects of the problem. Measurements were made on the heat evolved, as well as on the hardness and solubility of the cured products. Several catalysts were used to prepare the resoles. Maximum physical properties were obtained with a resole prepared from phenol using a phenol-formaldehyde ratio of 1:1.5 with NaOH as catalyst. If complete hardening occurs at formaldehyde ratios of greater than 1:1.5, the extra formaldehyde must be split out of the resin or ether linkages must be formed.

A general discussion of acid hardening has also been given by Scheiber and Barthel.¹⁶¹

C. CURE OF TWO-STAGE RESINS

The phenolic component of a Two-Stage resin is a novolac resin (see Chapter 4). This resin, as already outlined, is permanently soluble and fusible and requires the addition of a curing agent in order for cure to be achieved. Although paraform and many other materials have been suggested as curing agents, hexamethylenetetramine (also called hexa and hexamine) has been found most satisfactory for molding resins.

It has been estimated that roughly 80% of the phenolic molding compounds produced to date have been of the Two-Stage type based on a novolac resin cured by the action of hexamethylenetetramine. In addition, hexa-cured resins find use as the binder for abrasive wheels, brake linings, wood waste, and foundry resins. Hexa is most frequently used with novolac resins based on phenol and formaldehyde, but it can also be used with phenolic resins derived from other phenols and other aldehydes.¹⁶²⁻¹⁶⁴

The widespread acceptance of the Two-Stage, hexa-cured resins for molding purposes may be traced to several factors. One of the most important is the rapidity with which cure may be attained, coupled with good rigidity in the molded part at elevated temperatures. This permits rapid molding cycles with a minimum of warpage when the part is ejected from the mold. It is also a great advantage to be able to prepare a stable, hard, grindable resin, e.g., the novolac, essentially free of water and unreacted phenol and formaldehyde without great danger of gelation of the resin. This is a serious problem in the manufacture of One-Stage molding resins. The Two-Stage resins, because of the absence of methylol groups, are not as susceptible to caking, particularly under conditions of high humidity, as the One-Stage resins. Two-Stage resins give molded parts with a good finish, and, because water is not evolved during cure, they have superior electrical properties.

Aylsworth¹⁶⁵ covered the use of hexa as a curing agent for novolac resins in patents which were issued in 1911 and 1912, yet little time was devoted to a study of the curing mechanism involved until about the time of World War II. The only exceptions of importance were the publications of Koebner^{25, 26} and of Redman, Weith, and Brock.¹⁶⁶ These workers found that nitrogen-free products may be obtained by heating hexa with an excess of phenol. On the basis of these discoveries it was generally assumed that the hexa functioned only as a source of methylene bridges, and the ammonia liberated was presumed to function as a catalyst for the reaction. Redman and his coworkers

also reported that products containing nitrogen may be formed in the reaction of hexa with phenol, but the exact structure of these nitrogenous products was not established. It may seem surprising that this very important observation was not given greater attention since as much as 50–75% of the nitrogen added as hexa to commercial resins may remain in the cured product. Progress in elucidating the mechanism of the hexa cure may be attributed to a number of workers, but particularly to Zinke,^{35, 36, 42, 86, 187–172} Zigeuner,^{173–176} Imoto,^{176–177} Hultzschi,^{40, 178–180} and their respective collaborators.

Redman was not the first to obtain products containing nitrogen by the reaction of phenols with hexa or with formaldehyde plus ammonia. As early as 1904, Betti¹⁸¹ obtained a crystalline compound, $N(CH_2C_{10}H_6OH)_3$, from β -naphthol, formaldehyde, and alcoholic ammonia. Marotta and Alessandrini¹⁸² claimed that α -naphthol gave a similar product. Shono¹⁸³ and Duff and Bills^{184–185} also isolated crystalline nitrogenous products. Bromomethyl phenols were reacted with ammonia and methylamine to give hydroxybenzylamines.^{178, 186} All these observations are largely of historical interest since their relation to the curing mechanism as applied to novolac resins was unknown.

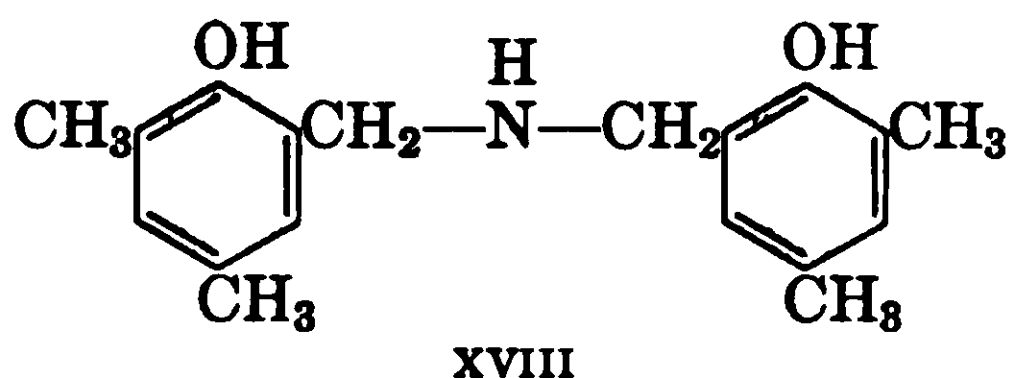
As in the studies on the cure of One-Stage resins, simplification of the systems was required before much progress could be made. The most satisfactory procedure was the use of mononuclear phenols, preferably with a single reactive position, in place of the novolac resins. Since many phenols form crystalline molecular addition compounds with hexa, a number of phenol-hexa complexes of phenols having a single reactive position were prepared and studied.

The phenol-hexa complexes are formed by mixing the phenol and hexa, each dissolved in an appropriate solvent, and allowing the complex to crystallize. With certain phenols the complex may be formed by simply grinding the phenol and hexa together in a mortar. Since the reaction is exothermic, care must be taken not to resinify the product. Phenol forms three complexes with hexa, having 1, 2, or 3 moles of phenol complexed with 1 mole of hexa. Many phenols combine in other ratios with hexa, and certain phenols do not form stable complexes with hexa.^{167, 187–191}

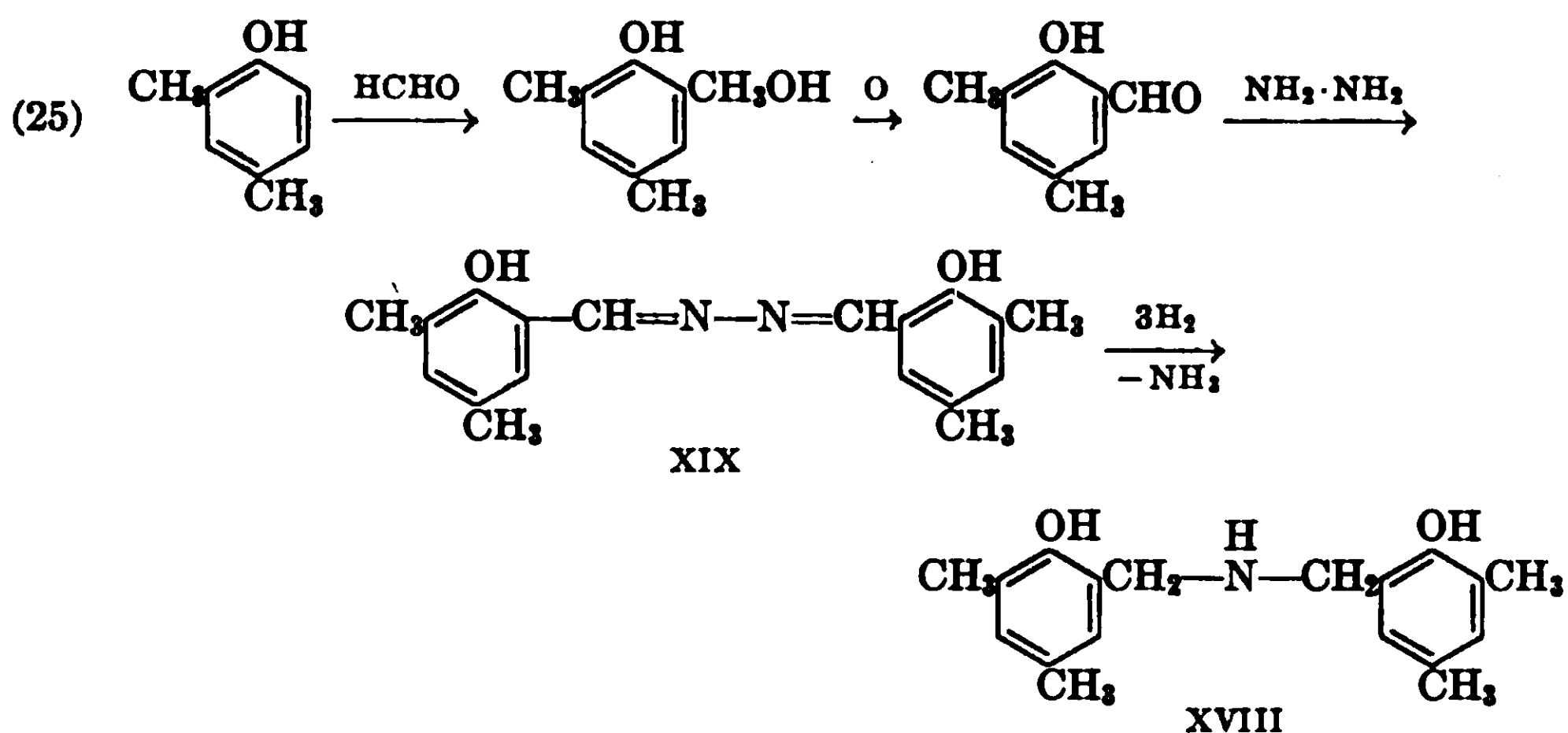
The studies with the phenol-hexa complexes were interesting, but it was soon found that mixtures of phenols with hexa gave essentially the same and frequently even more reproducible results.¹⁶⁷ Therefore the use of the complexes was dropped. It is now thought that the phenol-hexa complexes are important to cure only in that they bring the reactants into very intimate contact.

In place of the phenol-hexa complexes, mixtures of monoreactive

phenols with various proportions of hexa were studied. These experiments revealed that hydroxybenzylamines are important products of the reaction. By heating 2,4-dimethylphenol with hexa at 130–140°C. Zinke¹⁶⁹ found that 2,2'-dihydroxy-3,3',5,5'-tetramethyldibenzylamine, XVIII, was formed. Several compounds with structures similar to



XVIII and a variety of functional derivatives of the compounds have been prepared in fair to excellent yield from phenols having free *ortho* positions.^{168,169,178} The structure of the amine shown above was confirmed by an independent synthesis. The reactions shown in equation 25 were used by Zinke and St. Pucker¹⁷¹ for the synthesis of



XVIII. The reduction of XIX was carried out in alcoholic solution using zinc and acetic acid according to a process described by Curtius and Franzen.¹⁹² Duff and Furness¹⁹⁸ have also described a process whereby compounds similar to XVIII can be prepared from a large variety of phenols in good yield. Their process involves heating phenols with hexa and boric acid in 2-ethoxy ethanol.

Phenols with reactive *para* hydrogens behave somewhat differently with hexa from those with active *ortho* hydrogens. When 2,6-xyleneol¹⁶⁹ was heated in the presence of a small quantity of hexa a crystalline product, was obtained. This material proved to be an addition product of hexa and the tris(hydroxybenzyl)amine, XX. The same prod-

of the reaction of phenol with hexa. The formation of the benzylamines requires a free phenolic hydroxyl group and a free *o*- or *p*-position. Anisole or mesitol is unreactive towards hexa. The amines do not react further with phenols if the phenolic hydroxyl group has been blocked (as in phenyl acetate, for example). The limited data now available also indicate that phenols with free *para* hydrogens show a tendency to form tris(hydroxybenzyl)amines whereas those with free *ortho* positions tend to form the bis(hydroxybenzyl)amines.¹⁶⁹ However, exceptions to this general observation have been reported. For example, 2,4-xyleneol will give a tris(hydroxybenzyl)amine under the proper conditions.¹⁷¹ This difference in the type of product generally formed may be associated in some way with the rate of cure of the isomeric dihydroxydiphenylmethanes with hexa. Bender and Farnham¹⁹⁴⁻¹⁹⁵ have found that 2,2'-dihydroxydiphenylmethane, as well as novolac resins high in the *o*-, *o*-methylene bridge structures, cure more rapidly with hexa than 2,4'- or 4,4'-dihydroxydiphenylmethane. (See page 104.)

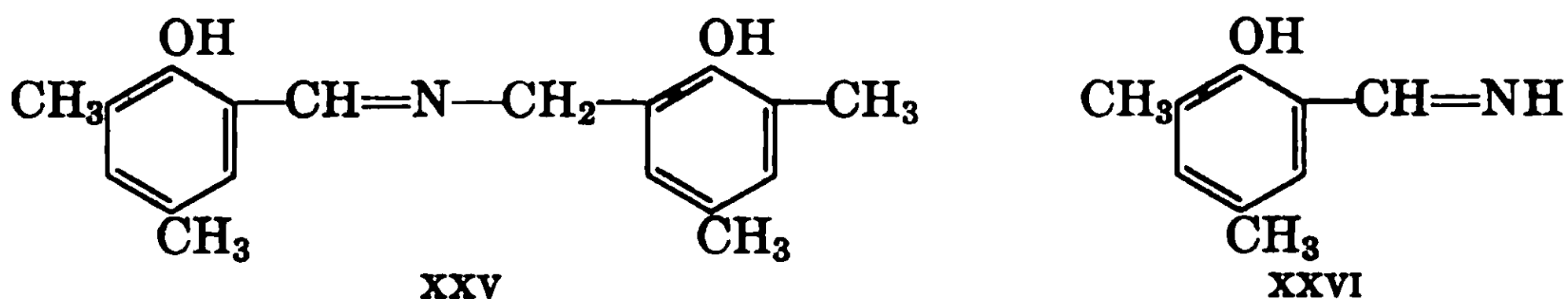
Many of the bis and tris(hydroxybenzyl)amines reported above were prepared by heating phenols with hexa at temperatures in the neighborhood of 130–140°C. or below. At higher temperatures, such as are often found during cure of Two-Stage resins, the hydroxybenzylamines appear to be subject to further reaction. In this respect they resemble the hydroxybenzyl ethers which were discussed earlier in this chapter.

Almost without exception the bis and tris(hydroxybenzyl)amines react with an excess of phenol to form nitrogen-free products. Even the complex polyamines such as XXIVa and XXIVb give nitrogen-free products upon heating with a phenol. The chief phenolic product of the reaction is a dihydroxydiphenylmethane. Müller and Müller¹⁹⁶ made use of the reaction of hydroxybenzylamines with phenols as a quantitative measure of the reactivity of resins prepared from phenol and hexa or from phenol and formaldehyde with ammonia as catalyst. (See also the results of Feldman and Wagner.¹⁹⁷)

If an excess of phenol is not present during the heating of the bis and tris(hydroxybenzyl)amines the reactions take a different course. When compounds XXIVa and XXIVb were heated alone at 180–190°C. for 7 hours, the nitrogen content of the products was still above 6%. The end product upon heating with phenol did not lose nitrogen quantitatively as it did before the heating. These results indicate that the amino bridges have gone over to products with other linkages which do not react with phenols. It now appears that the new linkage is probably an azomethine. This belief is supported by the fact that

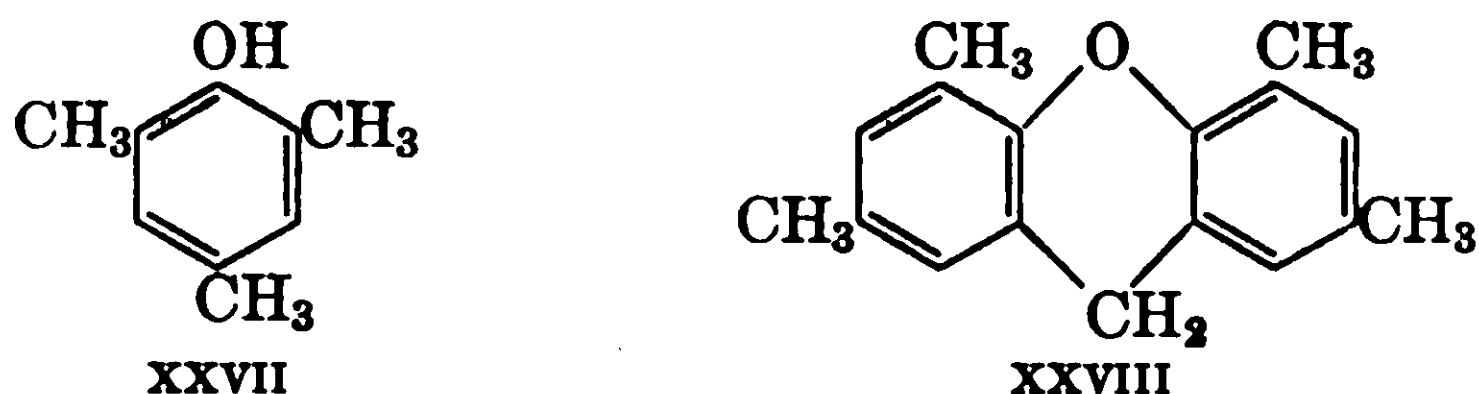
the product, on splitting with aqueous hydrochloric acid, gives an aldehyde.

The formation of an azomethine linkage from a hydroxybenzylamine was demonstrated conclusively in one example by Zinke¹⁶⁸ by the isolation of XXV from among the products obtained by heating XVIII



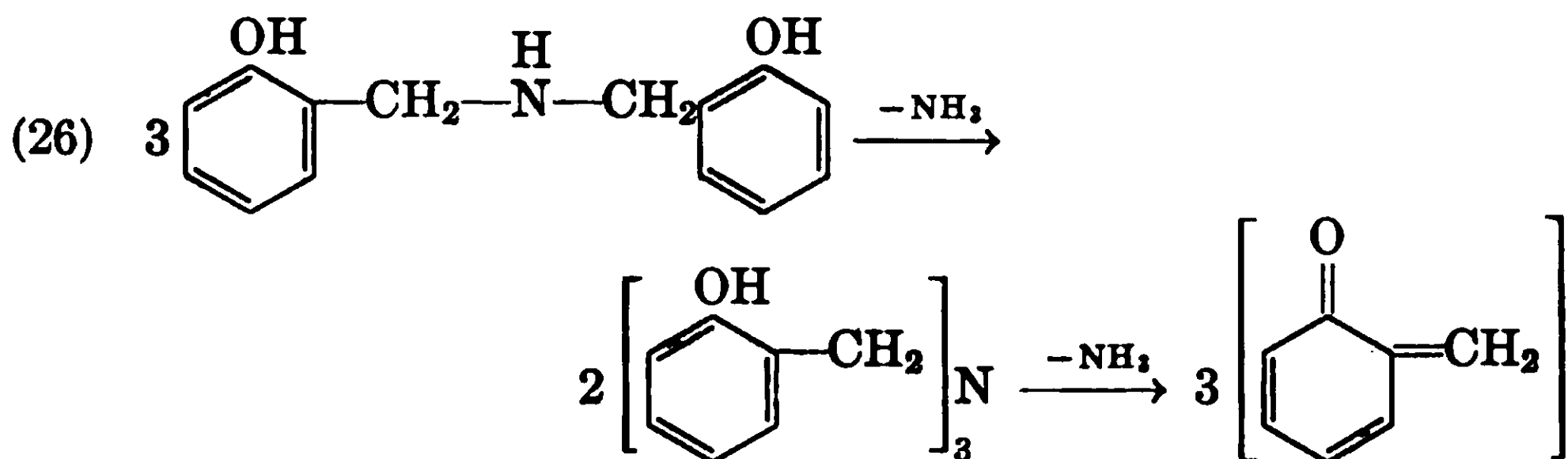
at a high temperature. The preparation of the mononuclear azomethine XXVI in pure form failed, but Hultzsche¹⁷⁸ obtained a yellow product which he thought might have been this compound. The azomethine linkage apparently is formed by a dehydrogenation reaction brought about by hexa. The dehydrogenating action of hexa on compounds such as XVIII has been utilized by Duff and Furness¹⁹⁸ to prepare a whole series of new Schiff's bases similar to XXV.

In addition to the azomethine linkages, other products may be formed upon heating hydroxybenzylamines to high temperatures. Zinke and St. Pucker,¹⁷¹ who studied the decomposition of the dihydroxydibenzylamine XVIII, found that ammonia started to come off at approximately 160–170°C., and upon raising the temperature further they obtained methylamine, mesitol XXVII, and tetramethylxanthene, XXVIII. The xanthene, undoubtedly, is formed by dehydration of



dihydroxytetramethyldiphenylmethane. If 2,4-xyleneol is mixed with the dihydroxydibenzylamine before the heating, dihydroxytetramethyldiphenylmethane and ammonia are formed.¹⁷⁰

One possibility not yet considered in the thermal decomposition of bis and tris(hydroxybenzyl)amines is the formation of quinone methides, reaction 26. All the polymerization and oxidation-reduction reactions of the quinone methides, as discussed for those derived from the decomposition of dibenzyl ethers, would be expected from the decomposition of the hydroxybenzylamines.



Summary

It has been found that hexa reacts with phenols and novolac resins to form bis and tris(hydroxybenzyl)amines or polynuclear derivatives of similar structure. Phenols with free *ortho* positions appear to form the secondary amine more readily; phenols with free *para* positions show a tendency to form more of the tertiary amines. The amine linkages in such products are unstable at high temperatures and may be converted to other linkages on further heating. If an excess of phenolic material is present, nitrogen-free products with the phenolic nuclei joined by methylene bridges will be formed. If an excess of phenolic material is not present, azomethine linkages may form and if the decomposition becomes extensive xanthene and methylphenols along with ammonia and methylamine will result. The products with an axomethine group are bright yellow bodies and may be responsible for much of the characteristic yellow color of hexa-cured resins.

D. HARDENING OF AMMONIA RESOLES

The reactions involved during the hardening of ammonia resoles are not yet thoroughly understood. Such resins are known to contain both phenol monoalcohols and phenol polyalcohols.¹⁹⁹ These phenol alcohols undoubtedly play a part in the cure of ammonia resoles. Bis- and tris(hydroxybenzyl)amines, which may form when phenols are heated with hexamethylenetetramine, are also present¹⁹⁹ and undoubtedly are responsible for part of the cure of resoles prepared with ammonia as catalysts. The relative importance of each one to cure is, as yet, unknown. Tsuruta²⁰⁰ thinks that an equilibrium probably exists between the phenol, formaldehyde, and ammonia and some intermediate whose structure he did not define. During cure the intermediate decomposes irreversibly to resin and ammonia.

E. OTHER CURING AGENTS

Numerous other compounds have been suggested as curing agents for novolac resins, such as quinone or chloranil,²⁰¹ anhydroformaldehyde-aniline,²⁰² and ethylene diamine-formaldehyde products.²⁰³ Methylol derivatives of both urea and melamine²⁰⁴ as curing agents for novolac resins have been covered in patents. The curing action of such compounds is associated with their reactive methylol groups. Diesbach^{205, 206} showed, for example, that dimethylol urea reacted with phenols to give bis(hydroxybenzyl) ureas. By substituting a novolac resin for the monomeric phenol, it is readily seen how cure might result. However, products cured in this manner would not be expected to have the thermal stability of resins cross-linked by methylene bridges. Martin²⁰⁷ obtained methylene derivatives when dimethylol urea was reacted with phenols under acidic conditions.

An important group of adhesives which set at room temperature are based on the cure of resorcinol resins with paraformaldehyde. Ordinarily paraformaldehyde or polyoxymethylene is a poor curing agent for novolac resins. However, if a low-molecular-weight novolac resin is prepared from resorcinol or a properly constituted resin from resorcinol and phenol the resin possesses sufficient activity to cure rapidly with paraform.^{182, 208} The mildly acid nature of resorcinol appears to be sufficient to cause the resin to function as its own catalyst. It is surprising to find that resorcinol resins cure poorly with hexa.

REFERENCES FOR CHAPTER 5

- ¹ H. von Euler, E. Adler, S. deKispeczy, and A. Fagerlund, *Arkiv Kemi Mineral. Geol.*, **A14**, No. 10, 1-20 (1940).
- ² T. S. Carswell, *Phenoplasts. Their Structure, Properties and Chemical Technology*, Interscience Publishers, New York, 1947.
- ³ C. Ellis, *The Chemistry of Synthetic Resins*, Reinhold Publishing Corp., New York, 1935.
- ⁴ K. Hultsch, *Chemie der Phenolharze*, Springer-Verlag, Berlin, 1950.
- ⁵ H. S. Lilley, *Brit. Plastics*, **19**, 346-347 (1947).
- ⁶ N. J. L. Megson, *Kunststoffe*, **38**, 76 (1948).
- ⁷ N. J. L. Megson, *Brit. Plastics*, **19**, 70-71 (1947).
- ⁸ L. H. Baekeland, *J. Ind. Eng. Chem.*, **1**, 545-549 (1909).
- ⁹ L. H. Baekeland, *J. Ind. Eng. Chem.*, **4**, 737-743 (1912).
- ¹⁰ R. Dubrisay and R. Papault, *Compt. rend.*, **215**, 348-350 (1942).
- ¹¹ A. Beatty, French pat. 447,648 (1912).
- ¹² J. P. Trickey, C. S. Miner, and H. J. Brownlee, *Ind. Eng. Chem.*, **15**, 65-66 (1923).
- ¹³ S. Sato, *J. Chem. Ind. Japan*, **24**, 586 (1921).
- ¹⁴ R. Dubrisay and R. Papault, *Inds. plastiques*, **1**, 132 (1945).

- ¹⁵ L. H. Baekeland, *J. Ind. Eng. Chem.*, **1**, 149-161 (1909).
¹⁶ H. Lebach, *Z. angew. Chem.*, **22**, 1598 (1909).
¹⁷ H. Lebach, *J. Soc. Chem. Ind.*, **32**, 559-664 (1913).
¹⁸ L. H. Baekeland, *J. Ind. Eng. Chem.*, **5**, 506 (1913).
¹⁹ F. Raschig, *Z. angew. Chem.*, **25**, 1947 (1912).
²⁰ F. Raschig, *Kunststoffe*, **27**, 51-55 (1937).
²¹ L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, **17**, 225-237 (1925).
²² A. E. Blumfeldt, *Chem. Ztg.*, **53**, 493-494 (1929).
²³ M. Koebner, *Brit. Plastics*, **11**, 7-9, 43 (1939).
²⁴ M. Koebner, *Brit. Plastics*, **14**, 95-101 (1942).
²⁵ M. Koebner, *Z. angew. Chem.*, **45**, 251-256 (1933).
²⁶ R. Barthel, Dissertation, Leipzig, 1936.
²⁷ N. J. L. Megson and A. A. Drummond, *J. Soc. Chem. Ind.*, **49**, 251-257T (1930).
²⁸ N. J. L. Megson, *Trans. Faraday Soc.*, **32**, 336 (1936).
²⁹ N. J. L. Megson, *J. Soc. Chem. Ind.*, **57**, 189-197 (1938).
³⁰ N. J. L. Megson, *J. Soc. Chem. Ind.*, **52**, 420-424T (1933).
³¹ N. J. L. Megson, *Brit. Plastics*, **9**, Note to editor (1937).
³² W. H. Carothers, "High Polymers," Vol. I, *Collected Papers of W. H. Carothers*, edited by H. E. Mark and G. S. Whitby, Interscience Publishers, New York, 1940.
³³ P. J. Flory, *J. Am. Chem. Soc.*, **59**, 466 (1937); **61**, 3334 (1939).
³⁴ A. Zinke, M. Tomio, and K. Lercher, *Ber.*, **75**, 151-155 (1942).
³⁵ A. Zinke, paper presented before Society of Chemical Industry, London, September, 1950.
³⁶ A. Zinke and E. Ziegler, *Fette u. Seifen*, **52**, 588-592 (1950).
³⁷ K. Hultsch, *Ber.*, **74B**, 898-904 (1941).
³⁸ E. Ziegler and I. Hontschik, *Monatsh.*, **78**, 325-333 (1948).
³⁹ K. Hultsch, *Kunststoffe*, **39**, 57-63 (1949).
⁴⁰ R. Castle, *Paint, Oil, and Colour J.*, **1951**, 493-495.
⁴¹ A. Zinke and E. Ziegler, *Wiener Chem. Ztg.*, **47**, 151-184 (1944).
⁴² A. Zinke, *J. Applied Chem.*, **1**, Pt. 6, 257-266 (1951).
⁴³ E. Schauenstein and S. Bontempo, *Ber.*, **75**, 75-80 (1943).
⁴⁴ H. von Euler, E. Adler, J. O. Cedwall, and O. Torngren, *Arkiv Kemi Mineral. Geol.*, **15A**, No. 11, 1-19 (1941).
⁴⁵ E. Imoto and T. Kimura, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **53**, 9-11 (1950).
⁴⁶ J. Reese, *Kunststoffe*, **45**, No. 4, 137-145 (1955).
⁴⁷ K. Hultsch, *Angew. Chem.*, **61**, 93-96 (1949).
⁴⁸ M. M. Sprung, *J. Am. Chem. Soc.*, **63**, 334-343 (1941).
⁴⁹ F. S. Granger, *Ind. Eng. Chem.*, **29**, 1305-1308 (1937).
⁵⁰ H. S. Lilley, *J. Oil Colour Chemists' Assoc.*, **26**, 88-95 (1943).
⁵¹ R. R. Whetstone, Brit. pat. 587,914 (1947).
⁵² J. J. Kessler, U. S. pat. 1,889,751 (1932).
⁵³ F. S. Granger, *Ind. Eng. Chem.*, **29**, 860, 1125 (1937).
⁵⁴ M. M. Sprung and M. T. Gladstone, *J. Am. Chem. Soc.*, **71**, 2907-2913 (1949).
⁵⁵ H. F. Müller and I. Müller, *Kunststoffe*, **42**, 57-63 (1952).
⁵⁶ A. A. Vanscheidt and A. A. Vaailiev, *J. Applied Chem. U.S.S.R.*, **19**, 7 (1946).

- ⁵⁵ E. Adler, H. von Euler, and J. O. Cedwall, *Arkiv Kemi Mineral. Geol.*, **A15**, No. 7, 1-17 (1941).
- ⁵⁷ H. von Euler, E. Adler, and J. O. Cedwall, *Arkiv Kemi Mineral. Geol.*, **A14**, No. 14A, 1-20 (1941).
- ⁵⁸ K. Fries and K. Kann, *Ann.*, **353**, 835-856 (1907).
- ⁵⁹ K. Hultsch, *Kunststoffe*, **37**, 205-208 (1947).
- ⁶⁰ R. W. Martin, *J. Am. Chem. Soc.*, **73**, 3952-3954 (1951).
- ⁶¹ J. H. Freeman and C. W. Lewis, *J. Am. Chem. Soc.*, **76**, 2080 (1954).
- ⁶² J. I. DeJong and J. DeJonge, *Rec. trav. chim.*, **71**, 643-660 (1952).
- ⁶³ T. Zincke and C. von Hohorst, *Ann.*, **353**, 357-379 (1907).
- ⁶⁴ J. I. DeJong and J. DeJonge, *Rec. trav. chim.*, **72**, 497 (1953).
- ⁶⁵ J. I. DeJong and J. DeJonge, *Rec. trav. chim.*, **71**, 661-667 (1952).
- ⁶⁶ H. Kammerer, *Makromolekulare Chem.*, **8**, Pt. 1, 85-96 (1952).
- ⁶⁷ H. Kammerer, *Makromolekulare Chem.*, **8**, Pt. 1, 98-109 (1952).
- ⁶⁸ Von Joh F. Ehlers, *Kolloid Z.*, **130**, Pt. 3, 161-165 (1953).
- ⁶⁹ G. Zigeuner and E. Ziegler, *Monatsh.*, **79**, 100 (1948).
- ⁷⁰ A. Greth, *Angew. Chem.*, **51**, 719 (1938).
- ⁷¹ F. Zipples, Dissertation, Tübingen, 1939.
- ⁷² R. W. Martin, unpublished work.
- ⁷³ H. von Euler, E. Adler, G. Eklund, and O. Torngren, *Arkiv Kemi Mineral. Geol.*, **B15**, No. 9, 1-7 (1942).
- ⁷⁴ S. Kyrning, *Arkiv Kemi Mineral. Geol.*, **B15**, No. 11, 1-8 (1941).
- ⁷⁵ K. Auwers and H. Ercklents, *Ann.*, **302**, 115 (1898).
- ⁷⁶ H. S. Lilley, *J. Soc. Chem. Ind.*, **67**, 196-199 (1948).
- ⁷⁷ P. Giocasa, *J. prakt. Chem.*, (2), **21**, 221 (1880).
- ⁷⁸ E. Ziegler and K. Lercher, *Ber.*, **74**, 841-844 (1941).
- ⁷⁹ K. Auwers and F. A. Traun, *Ber.*, **32**, 3309 (1899).
- ⁸⁰ K. Auwers and F. Baum, *Ber.*, **29**, 2338-2348 (1896).
- ⁸¹ K. Auwers et al., *Ber.*, **32**, 2978-2987, 3016-3033, 3454-3465 (1899).
- ⁸² A. Zinke, F. Hanus, and E. Ziegler, *J. prakt. Chem.*, (2), **152**, 126-144 (1939).
- ⁸³ F. Hanus and E. Fuchs (assisted by E. Ziegler), *J. prakt. Chem.*, (2), **152**, 327-336 (1939).
- ⁸⁴ K. Hultsch, *Kunststoffe*, **32**, 3 (1942).
- ⁸⁵ E. Adler and S. Kyrning, *Svensk Kem. Tid.*, **53**, No. 1, 5-11 (1940).
- ⁸⁶ A. Zinke, E. Ziegler, with I. Hontschik, *Monatsh.*, **78**, 317-324 (1946).
- ⁸⁷ F. Hanus assisted by K. Lercher, *J. prakt. Chem.*, (2), **158**, 245-253 (1941).
- ⁸⁸ S. Kyrning, *Arkiv Kemi Mineral. Geol.*, **A15**, No. 2, 1-9 (1941).
- ⁸⁹ E. Adler, *Arkiv Kemi Mineral. Geol.*, **B14**, No. 23, 1-7 (1941).
- ⁹⁰ E. Adler, H. von Euler, and H. G. Hasselquist, *Arkiv Kemi Mineral. Geol.*, **B14**, No. 24, 1-8 (1941).
- ⁹¹ A. T. Carpenter and R. F. Hunter, *J. Applied Chem.*, **1**, Pt. 5, 217-226 (1951).
- ^{91a} S. R. Finn, J. W. James, and C. J. S. Standen, *J. Applied Chem.*, **4**, 296-300 (1954).
- ⁹² H. S. Lilley and D. W. J. Osmond, *J. Soc. Chem. Ind.*, **66**, 425-427 (1947).
- ⁹³ E. G. K. Pritchett, *Chemistry & Industry*, 295-299 (1949)
- ⁹⁴ K. Hultsch, *Ber.*, **74**, 1533-1538 (1941).
- ⁹⁵ E. Ziegler and R. Kohlhauser, *Monatsh.*, **79**, 92-99 (1948).
- ⁹⁶ A. Zinke and E. Ziegler, *Ber.*, **74**, 541-545 (1941)
- ⁹⁷ A. Zinke, E. Ziegler, et al., *Ber.*, **77**, 264-272 (1944)

- ⁹⁸ H. L. Bender et al., Preprint *Bull., Div. Paint, Varnish, and Plastics Chem., Am. Chem. Soc.*, September, 1960, pp. 73-77.
- ⁹⁹ R. Barthel, *Plastica (Holland)*, **2**, 247-251 (1949).
- ¹⁰⁰ K. Hultsch, *J. prakt. Chem.*, **159**, 155-179 (1942).
- ¹⁰¹ R. Wegler and K. Faber, *Chem. Ber.*, **82**, 327 (1949).
- ¹⁰² A. Zinke and E. Ziegler, *Ber.*, **74**, 1729-1736 (1941).
- ¹⁰³ R. W. Martin, *Anal. Chem.*, **23**, 883-884 (1961).
- ¹⁰⁴ E. Adler, S. Tingstam, and A. O. Caspersson, *Arkiv Kemi Mineral. Geol.*, **B15**, No. 10, 1-8 (1942).
- ¹⁰⁵ A. Zinke, F. Hanus, et al., *Ber.*, **74B**, 205-214 (1941).
- ¹⁰⁶ K. Hultsch, *Kunststoffe*, **32**, 69-76 (1942).
- ¹⁰⁷ H. von Euler, E. Adler, and S. Tingstam, *Arkiv Kemi Mineral. Geol.*, **A15**, No. 10, 1-11 (1941).
- ¹⁰⁸ H. von Euler, E. Adler, and B. Bergstrom, *Arkiv Kemi Mineral. Geol.*, **B14**, No. 25, 1-6 (1941).
- ¹⁰⁹ H. von Euler, *Angew. Chem.*, **54**, 458 (1941).
- ¹¹⁰ J. Thiele and O. Dimroth, *Ann.*, **305**, 102 (1899).
- ¹¹¹ H. Pauly and R. F. V. Brittlar, *Ann.*, **383**, 230-288 (1911).
- ¹¹² E. F. Pratt, R. K. Preston, and J. D. Draper, *J. Am. Chem. Soc.*, **72**, 1367-1369 (1950).
- ¹¹³ Yu. S. Zalking and I. P. Kurlina, *J. Gen. Chem. U.S.S.R.*, **20**, 2239 (1950).
- ¹¹⁴ E. Mayer-Pitsch and H. Tröger, *Z. Elektrochem.*, **47**, 60-65 (1941).
- ¹¹⁵ K. Hultsch and G. Schiemann, *Ber.*, **75**, 363-368 (1942).
- ¹¹⁶ K. Hultsch, *Ber.*, **75B**, 106-114 (1942).
- ¹¹⁷ S. Cannizaro, *Ann.*, **92**, 116 (1854).
- ¹¹⁸ A. Wohl and B. Mylo, *Ber.*, **45**, 2046 (1912).
- ¹¹⁹ J. Novak and V. Cech, *Ind. Eng. Chem.*, **20**, 796 (1928).
- ¹²⁰ K. Auwers and H. Burrows, *Ber.*, **32**, 3034-3045 (1899).
- ¹²¹ K. Auwers, *Ber.*, **36**, 1878 (1903).
- ¹²² K. Auwers, *Ber.*, **40**, 2524-2537 (1907).
- ¹²³ K. Auwers, F. A. Traun, and R. Welde, *Ber.*, **32**, 3297-3309 (1899).
- ¹²⁴ Th. Zincke, *Ann.*, **343**, 10-108 (1905).
- ¹²⁵ K. Fries and F. Brandes, *Ann.*, **542**, 48 (1939).
- ¹²⁶ K. Fries and F. Struffmann, *Ann.*, **542**, 55-56 (1939).
- ¹²⁷ K. Fries and E. Hubner, *Ber.*, **39**, 435 (1906).
- ¹²⁸ K. Hultsch, *J. prakt. Chem.*, **158**, 276-294 (1941).
- ¹²⁹ K. Hultsch, *Angew. Chem.*, **A60**, 179-184 (1948).
- ¹³⁰ K. Hultsch, *Kunststoffe*, **39**, 192 (1949).
- ¹³¹ K. Hultsch, *Ber.*, **74**, 1539-1543 (1941).
- ¹³² K. Hultsch, *Kunststoffe*, **41**, 109-116 (1961).
- ¹³³ H. von Euler, E. Adler, H. Hasselquist, and M. Lundin, *Arkiv Kemi Mineral. Geol.*, **18A**, No. 7, 1-23 (1944).
- ¹³⁴ H. von Euler, E. Adler, and A. O. Caspersson, *Arkiv Kemi Mineral. Geol.*, **A16**, No. 11, 1-14 (1943).
- ¹³⁵ R. Pummerer and E. Cherbuliez, *Ber.*, **52**, 1392 (1919).
- ¹³⁶ H. S. Lilley, *J. Soc. Chem. Ind.*, **67**, 196-199 (1948).
- ¹³⁷ G. Schiemann and K. Hultsch, *Naturwissenschaften*, **35**, 124 (1948).
- ¹³⁸ C. A. Redfarn, *Brit. Plastics*, **14**, 136 (1942).
- ¹³⁹ C. A. Redfarn, *Brit. Plastics*, **19**, 15, 152 (1947).

- ¹⁴⁰ R. F. Bowles, comments on lecture by C. A. Redfarn before Chemical Society, London, October, 1941; *Chem. Ind.*, 1941, 866.
- ¹⁴¹ R. Pummerer, G. Schmidutz, and H. Seifert, *Ber.*, 85, 535 (1952).
- ¹⁴² S. R. Finn, N. J. L. Megson, and E. J. W. Whittaker, *Chemistry & Industry*, 1950, S849-S853.
- ¹⁴³ R. W. Martin, paper presented before American Chemical Society Meeting, Div. of Polymer Chemistry, Atlantic City, September, 1952.
- ¹⁴⁴ H. Nickerson, *Brit. Plastics*, 19, 345 (1947).
- ¹⁴⁵ E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 58, 63-65 (1950).
- ¹⁴⁶ W. Charlton and L. E. Perrins, *J. Oil & Colour Chemists' Assoc.*, 30, No. 324, 185 (1947).
- ¹⁴⁷ H. L. Bender, et al., *Ind. Eng. Chem.*, 44, 1619 (1952).
- ¹⁴⁸ N. J. L. Megson, *J. Soc. Chem. Ind.*, 67, 156-150 (1948).
- ¹⁴⁹ N. J. L. Megson, paper presented at International Congress on Plastics in Paris, January, 1949.
- ¹⁵⁰ H. Lebach, *J. Soc. Chem. Ind.*, 28, 803 (1909).
- ¹⁵¹ T. T. Jones, *J. Soc. Chem. Ind.*, 65, 264-275 (1946).
- ¹⁵² G. E. Little and K. W. Pepper, *Brit. Plastics*, 19, 430 (1947).
- ¹⁵³ Aero Research Ltd., Oxford, England, *Sci. and Tech. Memo*, December, 1946, pp. 1-47.
- ¹⁵⁴ A. Lewin and P. Robitachek, *Brit. Plastics*, 17, 316-322, 385-391 (1945).
- ¹⁵⁵ J. J. Smith, F. M. Rugg, and H. M. Bowman, *Anal. Chem.*, 24, 497 (1952).
- ¹⁵⁶ H. F. Müller and I. Müller, *Kunststoffe*, 87, 75 (1947).
- ¹⁵⁷ L. M. Pesin and Ch. G. Khasanor, *Org. Chem. Ind. U.S.S.R.*, 7, 314-317 (1940).
- ¹⁵⁸ J. D. Nelson and P. V. Steenstrup, U. S. pat. 2,446,429 (1948).
- ¹⁵⁹ A. A. J. Sigtermans, *Polytech. Tijdschr.*, 5, 370a-372a (1950).
- ¹⁶⁰ R. A. Glauret, *Brit. Plastics*, 19, 333-339 (1947).
- ¹⁶¹ J. Scheiber and R. Barthel, *J. prakt. Chem.*, 147, 99-109 (1936).
- ¹⁶² I. P. Losev, V. M. Kotrelov, and A. Ya Fegina, *Org. Chem. Ind. U.S.S.R.*, 3, 558-561 (1937).
- ¹⁶³ G. R. Owens, U. S. pat. 2,458,408 (1948).
- ¹⁶⁴ J. McIntosh, *Ind. Eng. Chem.*, 19, 111 (1927).
- ¹⁶⁵ J. W. Aylsworth, U. S. pat. 1,102,594 (1912); Brit. pat. 3,496 (1911).
- ¹⁶⁶ L. V. Redman, A. J. Weith, and F. P. Brock, *Ind. Eng. Chem.*, 6, 3 (1914).
- ¹⁶⁷ A. Zinke, F. Hanus, and H. Pichelmayer, *Monatsh.*, 78, 311-316 (1948).
- ¹⁶⁸ A. Zinke, G. Zigeuner, and G. Weiss, *Monatsh.*, 80, 148-150 (1949).
- ¹⁶⁹ A. Zinke, G. Zigeuner, G. Weiss, and E. Wiesenberger, *Monatsh.*, 80, 160-169 (1949).
- ¹⁷⁰ A. Zinke, G. Zigeuner, G. Wiesz, and W. Schaden, *Monatsh.*, 81, 999-1006 (1950).
- ¹⁷¹ A. Zinke and St. Pucker, *Monatsh.*, 79, 26-41 (1948).
- ¹⁷² A. Zinke, G. Zigeuner, G. Weiss, and W. Leupold-Löwenthal, *Monatsh.*, 81, 1098-1107 (1950).
- ¹⁷³ G. Zigeuner and W. Schaden, *Monatsh.*, 81, 1017-1023 (1950).
- ¹⁷⁴ G. Zigeuner and O. Gabriel, *Monatsh.*, 81, 952-953 (1950).
- ¹⁷⁵ G. Zigeuner, W. Schaden, and O. Gabriel, *Monatsh.*, 81, 1108-1112 (1950).
- ¹⁷⁶ E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 52, 242-244 (1949).
- ¹⁷⁷ E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 52, 185-188, 188-189 (1949).

- ¹⁷⁸ K. Hultzsich, *Ber.*, **82**, 16-25 (1949).
¹⁷⁸ K. Hultzsich, *Angew. Chem.*, **63**, 168-171 (1951).
¹⁸⁰ K. Hultzsich, *Kunststoffe*, **41**, 109, 116 (1951).
¹⁸¹ M. Betti, *Gaz. chim. ital.*, **30** II, 310 (1900); **31** I, 377 (1901); **31** II, 170 (1901); **34**, 212 (1904).
¹⁸² D. Marotta and M. E. Alessandrini, *Gaz. chim. ital.*, **61**, 977 (1931).
¹⁸⁸ T. Shono, *J. Chem. Ind. Japan*, **29**, 53, 438 (1926); **30**, 136 (1927); **32**, 212 (1929).
¹⁸⁴ J. C. Duff and E. J. Bills, *J. Chem. Soc.*, **1932**, 1987.
¹⁸⁸ J. C. Duff and E. J. Bills, *J. Chem. Soc.*, **1934**, 1305-1308.
¹⁸⁸ K. Auwers and C. Kipke, *Ann.*, **343**, 200 (1905).
¹⁸⁷ L. H. Smith and K. N. Welch, *J. Chem. Soc.*, **1934**, 729.
¹⁸⁸ R. Pummerer and J. Hoffman, *Ber.*, **56**, 1255 (1923).
¹⁸⁹ H. Moschatos and B. Tollens, *Ann.*, **272**, 271 (1892).
¹⁹⁰ M. Harvey and L. H. Baekeland, *Ind. Eng. Chem.*, **13**, 135 (1921).
¹⁹¹ S. Kambara and H. Tada, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **53**, 163-166 (1950).
¹⁹² Th. Curtius and H. Franzen, *Ber.*, **34**, 553 (1901).
¹⁹⁸ J. C. Duff and V. I. Furness, *J. Chem. Soc.*, **1951**, 1512-1515.
¹⁹⁴ H. L. Bender and A. G. Farnham, U. S. pat. 2,475,587 (1949).
¹⁹⁸ H. L. Bender, *Modern Plastics*, February, 1953, 136.
¹⁹⁶ H. F. Müller and I. Müller, *Kunststoffe*, **41**, 186-188 (1951).
¹⁹⁷ J. R. Feldman and E. C. Wagner, *J. Org. Chem.*, **7**, 31-47 (1942).
¹⁹⁸ R. W. Martin, *J. Am. Chem. Soc.*, **70**, 4208 (1952).
¹⁹⁹ S. Seto, in press.
²⁰⁰ S. Tsuruta, *J. Soc. Chem. Ind., Japan*, **44**, 57-58 (1941).
²⁰¹ F. Seebach, U. S. pat. 1,883,145 (1932).
²⁰² L. H. Baekeland, U. S. pat. 1,216,265 (1917).
²⁰⁸ Clopay Corporation.
²⁰⁴ F. J. Groten, U. S. pat. 2,287,256 (1943).
²⁰⁸ H. von Diesbach, Ger. pat. 611,210 (1930).
²⁰⁸ H. von Diesbach, O. Wanger, and A. von Stockalper, *Helv. Chim. Acta*, **14**, 355 (1931).
²⁰⁷ R. W. Martin, *J. Org. Chem.*, **17**, 342 (1952).
²⁰⁸ E. E. Novotny, U. S. pats. 1,767,696 (1930); 1,802,390 (1931); 1,849,109 (1932).

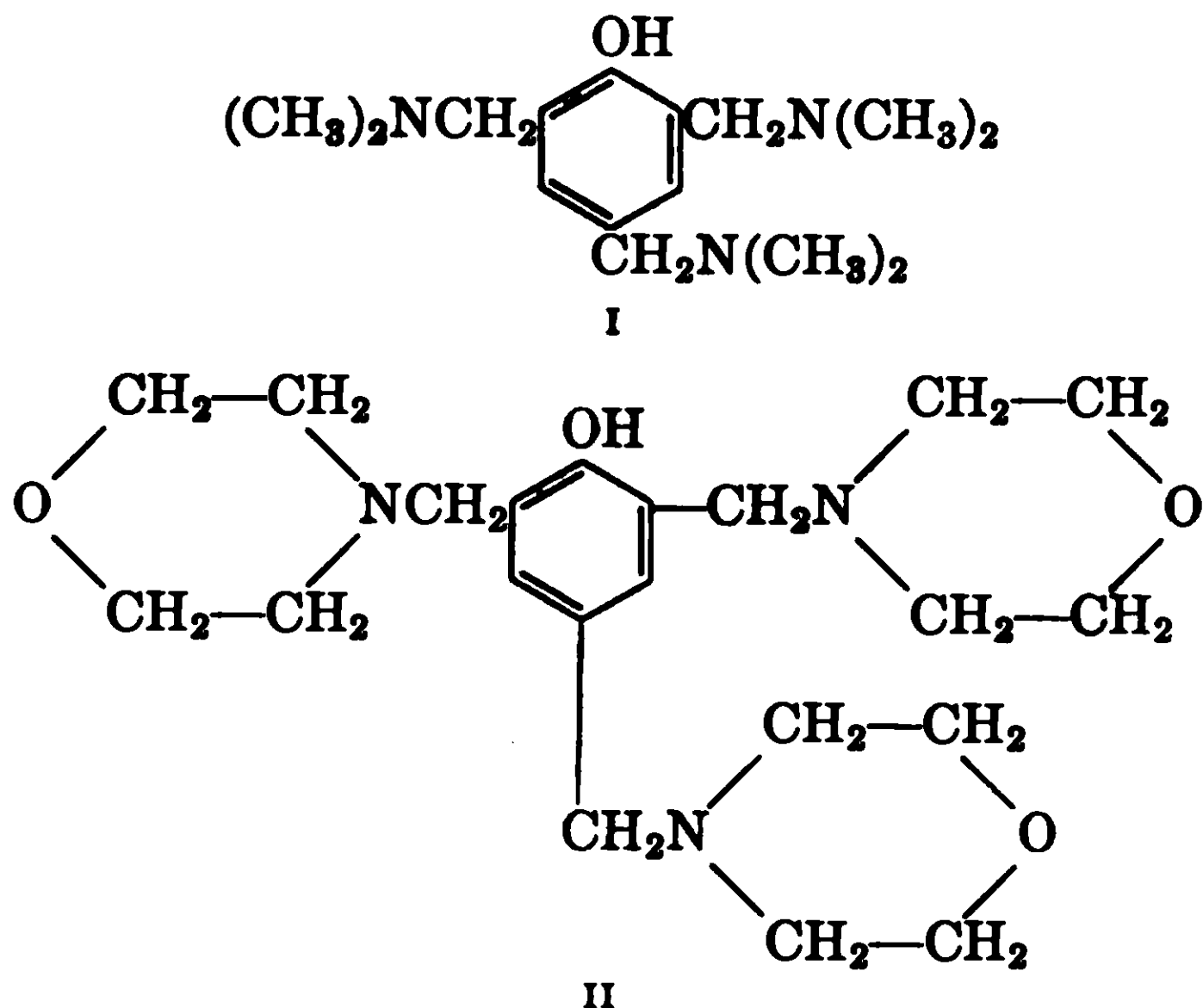
C H A P T E R S I X

Joint Reactions of Phenols and Aldehydes with an Added Reagent

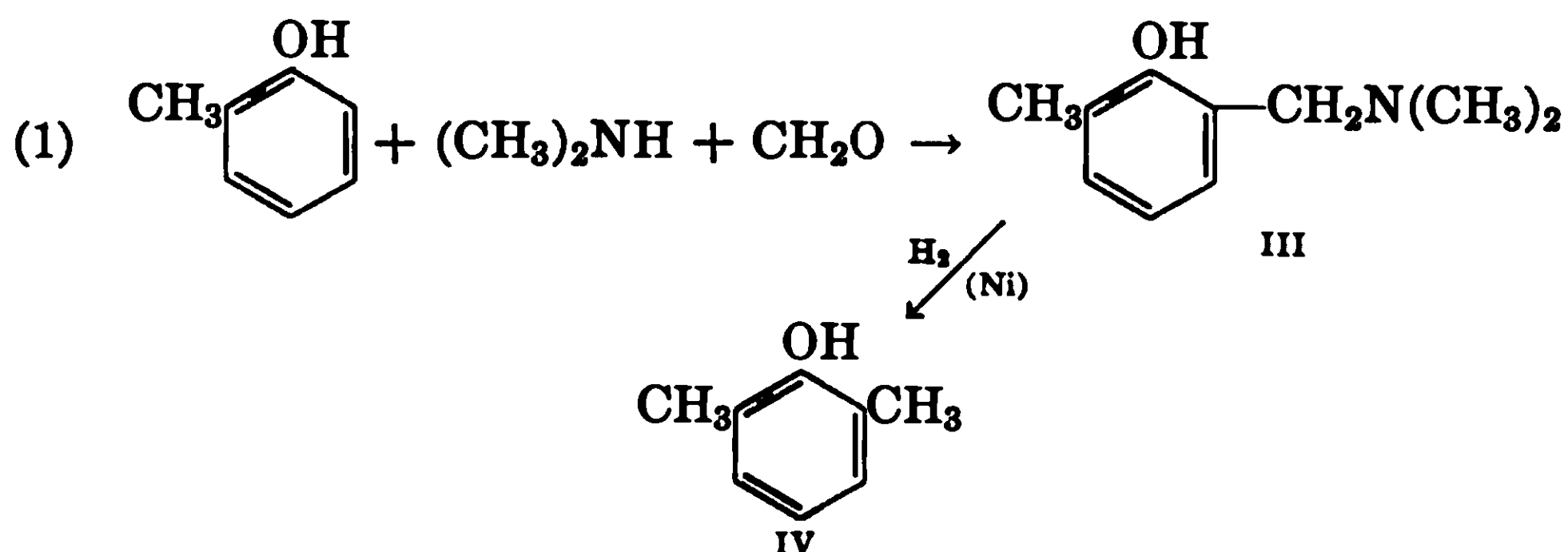
Phenols and aldehydes frequently undergo joint reactions with a third reagent to yield products that may be difficult or impossible to obtain in a stepwise fashion. For simplicity of treatment these reactions have been grouped together for separate consideration. The reactions where cyclic products are formed are discussed in Chapter Seven. The formation of alkylaminomethyl derivatives, phenolic-type Mannich bases, and the halomethyl phenols are the most common examples of such reactions.

MANNICH REACTION WITH PHENOLS

The Mannich reaction, which consists in the joint condensation of ammonia or a primary or secondary amine and an aldehyde with a compound having a reactive hydrogen atom, was discovered by Tollens^{1,2} and later studied in detail by Mannich.³ Phenols are only one of a group of compounds possessing the necessary active hydrogen atoms.^{4,6} The reaction results in the replacement of the active hydrogen atom by an aminomethyl or a substituted aminomethyl group. In the case of phenols the secondary amines are most useful. With such amines, reaction may occur at all the positions *ortho* or *para* to the phenolic group, as was shown by the preparation of I and II by Bruson and MacMullen.⁶ The preparation of I was carried out by dissolving a mole of phenol in 720 grams of 25% aqueous dimethylamine and cooling to 20°C. The temperature was maintained at 25–30°C., and 350 grams of 30% aqueous formalin was added dropwise over a period of 30 minutes. The temperature was held at 25–30°C. for an additional half hour. Reaction was completed by heating on a steam bath for 2 hours. The yield of isolated product was 86% of theory. Compound II, m.p. 107–8°C., is readily prepared in alcoholic solution.

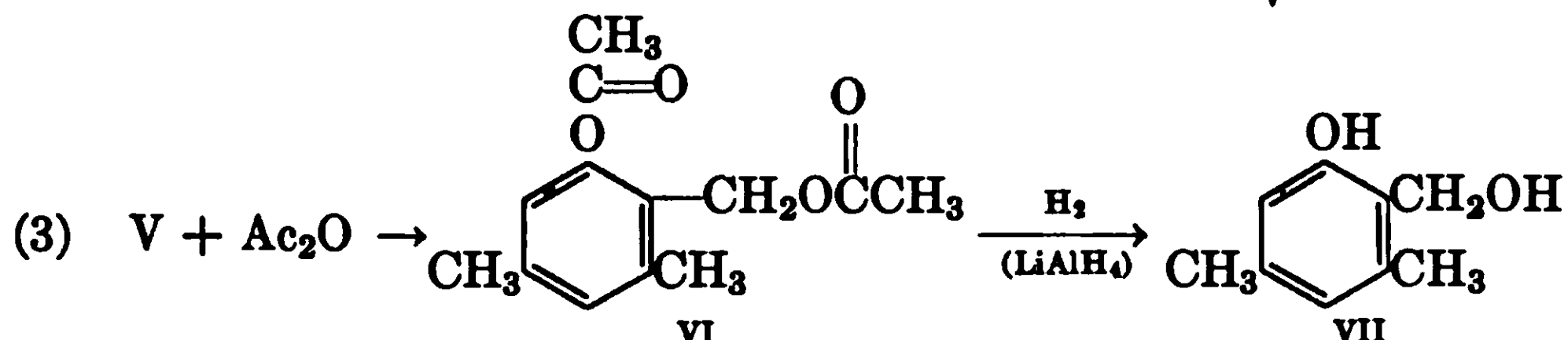
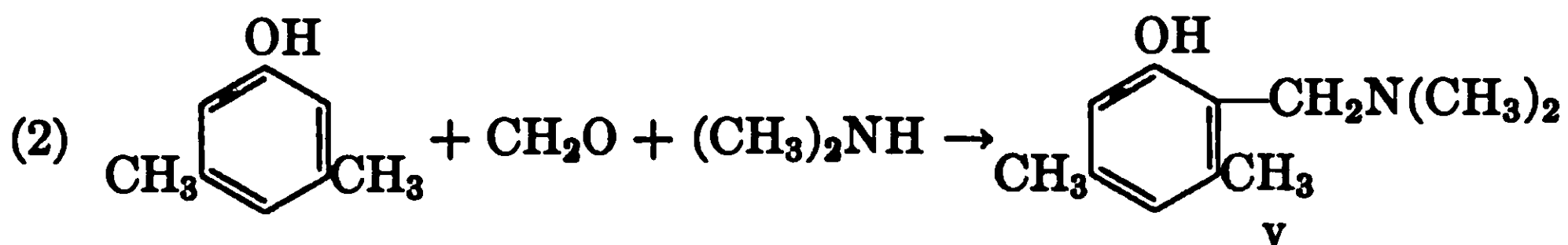


A wide variety of phenols and amines have been subjected to the Mannich reaction.⁷⁻²⁶ Where both an *ortho* and a *para* position are available, reaction ordinarily occurs first at the *ortho* position, although exceptions may be found.^{11, 16, 27} The tendency for the substituted aminomethyl group to enter an *ortho* position is often utilized to advantage in preparative work. For example, Carlin and Landerl¹⁶ prepared 2,6-xylenol, IV, from *o*-cresol by the reactions shown in equation 1. By a similar procedure, Caldwell and Thompson prepared



2,3,5-trimethylphenol from 3,5-xylenol, and 2,5-dimethylhydroquinone from hydroquinone.

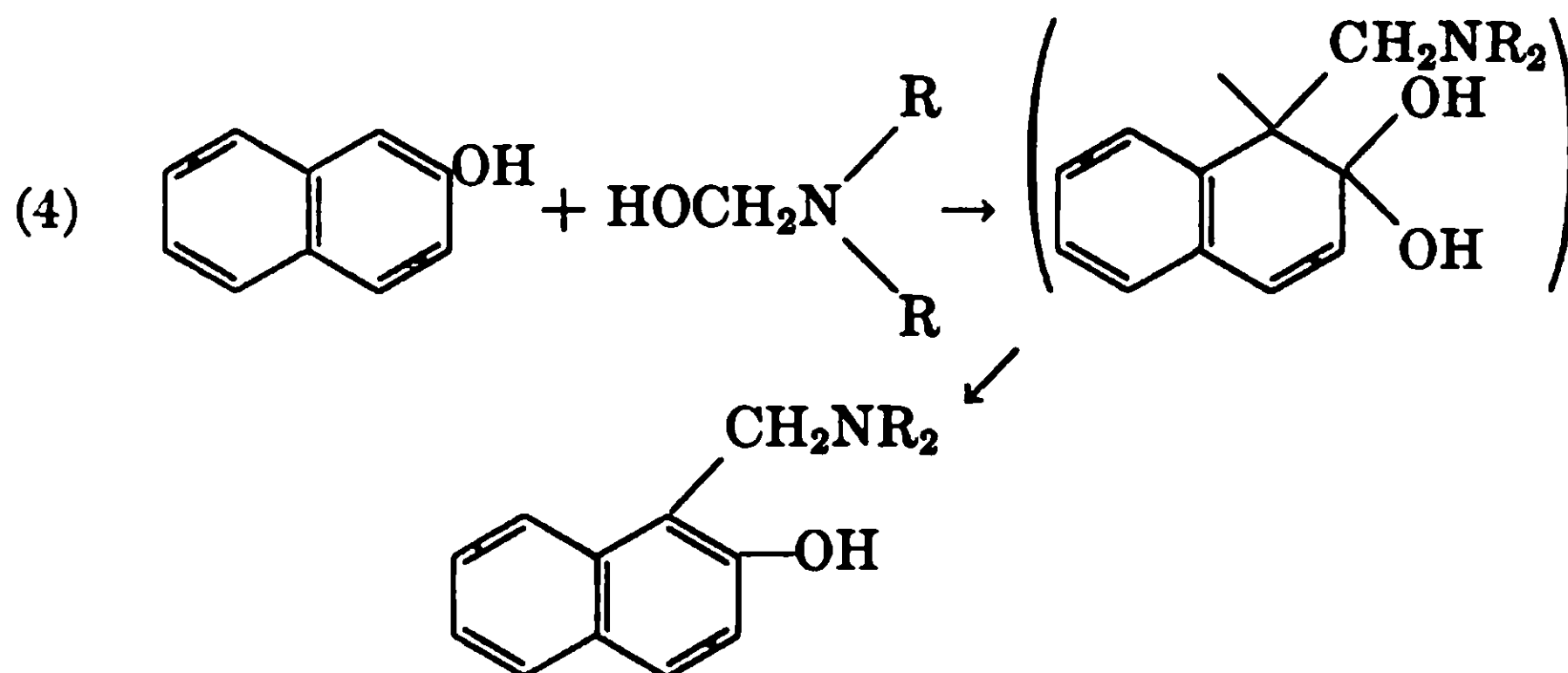
An elegant procedure for the preparation of *ortho*-phenol alcohols has been described by Finn and Musty.^{28, 29} The preparation of VII illustrates the reactions used, reactions 2 and 3. Compound V was obtained in approximately 45% yield after purification. The reaction



of compounds such as V with acid anhydrides was discovered by Bruson MacMullen.^{6, 30}

Not all phenols undergo the Mannich reaction; others react only once even though more than one *ortho* or *para* position may be available. Caldwell and Thompson¹¹ were unable to introduce two dimethylaminomethyl or two morpholinomethyl groups into 3,5-xylenol. However, 2,3,5-trimethylphenol reacted readily. Obviously, steric factors alone cannot explain their results. Only one group could be introduced into 2,5-dimethylhydroquinone or 3,4-dimethyl-6-isopropylphenol, although the former has two reactive hydrogen atoms. 2,3,5,6-Tetramethylphenol failed to react. Thymol, quite unexpectedly, reacted only at the *para* position.

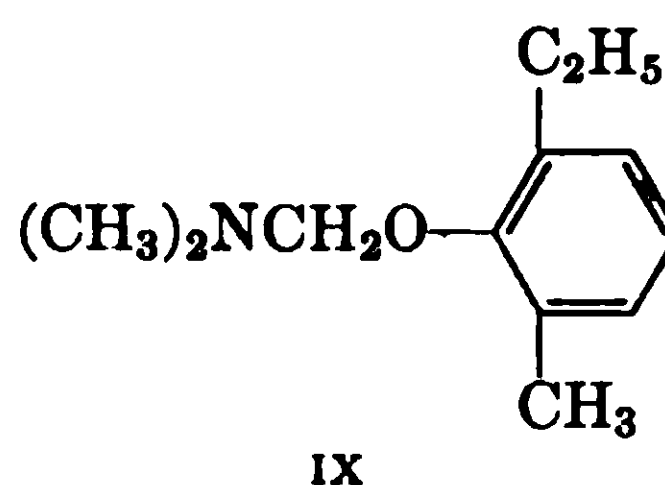
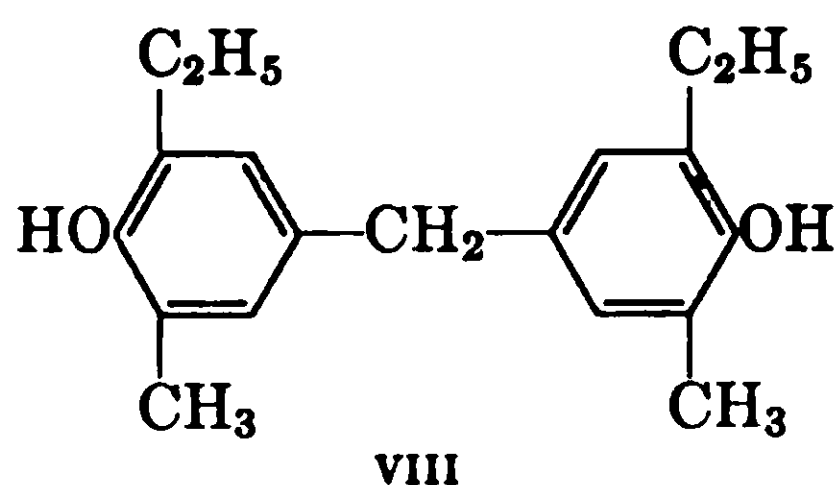
The mechanism of the Mannich reaction has been much debated. Caldwell and Thompson¹¹ consider that the reaction involves the formation of a substituted methylolamine which then condenses with the phenol. The alternative mechanism, where a methylolphenol is first formed and then reacts with the amine, was rejected since they were unable to effect reaction between *p*-cresol dialcohol and a secondary amine under conditions normally employed for the Mannich reaction. However, Jones³¹ succeeded in causing reaction between a phenol alcohol and a secondary amine using an acidic catalyst. With β -naphthol Caldwell and Thompson formulated the reaction as shown in equation 4. Bruson has expressed similar views,²² but Bodendorf and Koralewski³² do not consider that methylol derivatives of either the amine or the active hydrogen compound, in this instance phenol, meet all the requirements of an intermediate, since they give subnormal yields of the Mannich base. More recently Lieberman and Wagner³³ have proposed the formation of methylene bis-amines as active intermediates but do not exclude possible formation of methylolamines. The reaction using the methylene bis-amines was promoted by catalytic amounts of acids or alkalies but was depressed by exces-



sive amounts of either. It is interesting to note that the methylene *bis*-amines when used in place of formaldehyde and amine gave normal yields of Mannich base with various phenols.^{33, 34}

Alexander and Underhill found that the Mannich reaction involving ethyl malonic acid, formaldehyde, and dimethylamine follows third-order kinetics.³⁵

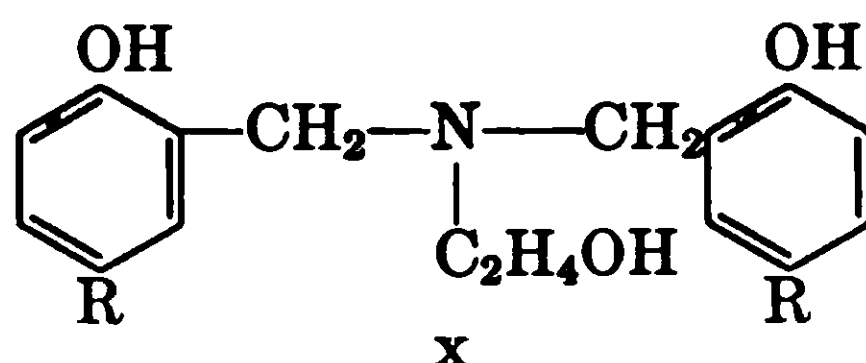
Early patent literature reported what appears to be an unusual reaction between 2-methyl-6-ethylphenol, formaldehyde, and dimethylamine. It was claimed that the reaction yielded a mixture of products, VIII and IX. Decombe¹⁰ repeated the experiments but was unable to detect the formation of IX. The structure assigned to IX



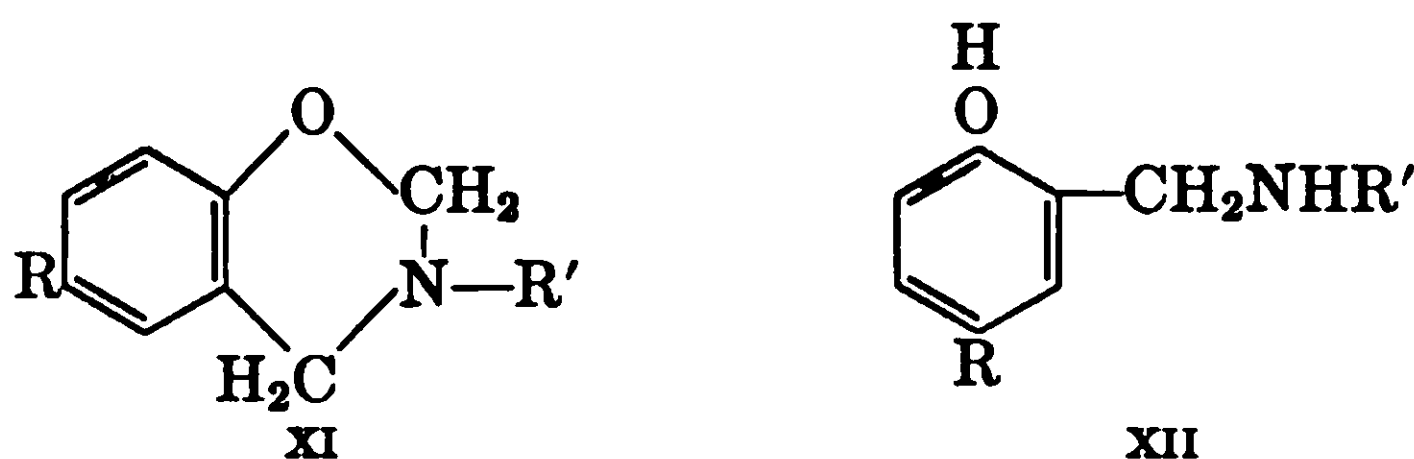
by the early workers was based largely on the alkali insolubility of the product. This argument may not be well founded since it is known that the phenolic character of di-*ortho*-substituted phenols may be almost completely masked by the two *ortho* substituents.

Primary amines will also undergo joint reactions with phenols and formaldehyde. Highly reactive phenols usually give only resins, but with substituted phenols resin formation may be minimized and crystalline products may be isolated. Bruson²² has studied the reaction of formaldehyde and ethanolamine with various phenols using equimolar proportions of the three reactants. Crystalline compounds which appear to contain the $-\text{CH}_2\text{NHC}_2\text{H}_4\text{OH}$ group attached to the

aromatic nucleus were obtained with some phenols. *p*-Phenylphenol and *p*-cyclohexylphenol gave crystalline compounds in which the nitrogen analysis indicated the presence of two phenolic nuclei in the products. A probable formula for the compounds is given in X.



Burke³⁶ studied the reaction of *para*-substituted phenols with formaldehyde and primary amines. In a molar ratio of 1:2:1, a new series of compounds, the 3,4-dihydro-3,6-disubstituted-1,3-2H-benzoxazines, XI, were obtained in good yield. The intermediate compound,



XII, gave XI on treatment with formaldehyde and a basic catalyst. Polyhydric phenols gave even more complex products.

The higher aldehydes, particularly those without α -hydrogens such as benzaldehyde, may be used in joint reactions with phenols and amines and with phenols and ammonia.³⁷ The reactions of phenols with ammonia and formaldehyde were covered in Chapter 5.

One amine group of a phenolic-type Mannich base may be exchanged for another amine group by heating with a higher-boiling amine.³⁸ This is a general reaction that often proceeds essentially quantitatively.

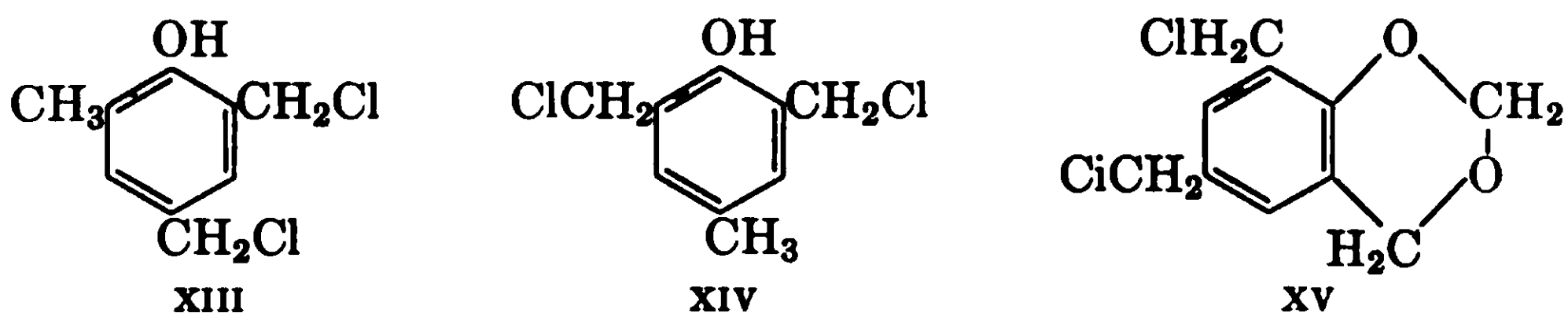
A number of phenolic-type Mannich bases are available commercially and have found a variety of industrial uses.^{39, 40}

HALOMETHYLATION OF PHENOLS

The replacement of a hydrogen atom of an aromatic compound by a halomethyl group in a single operation by the joint reaction with an aldehyde and a halogen acid is known as halomethylation.⁴ The reaction was discovered by Grassi and Maselli⁴¹ in 1898 and was first applied to the chloromethylation of benzene. With phenols the reac-

tion often proceeds with such vigor that either dihydroxydiphenylmethanes or resin is formed spontaneously. However, the tendency towards condensation is less noticeable with the *o*- and *p*-alkyl or negatively substituted phenols, and the halomethyl derivatives of such compounds can often be obtained in good yield provided that proper precautions are observed. A wide variety of phenols have been subjected to the halomethylation reaction.^{26, 42-59}

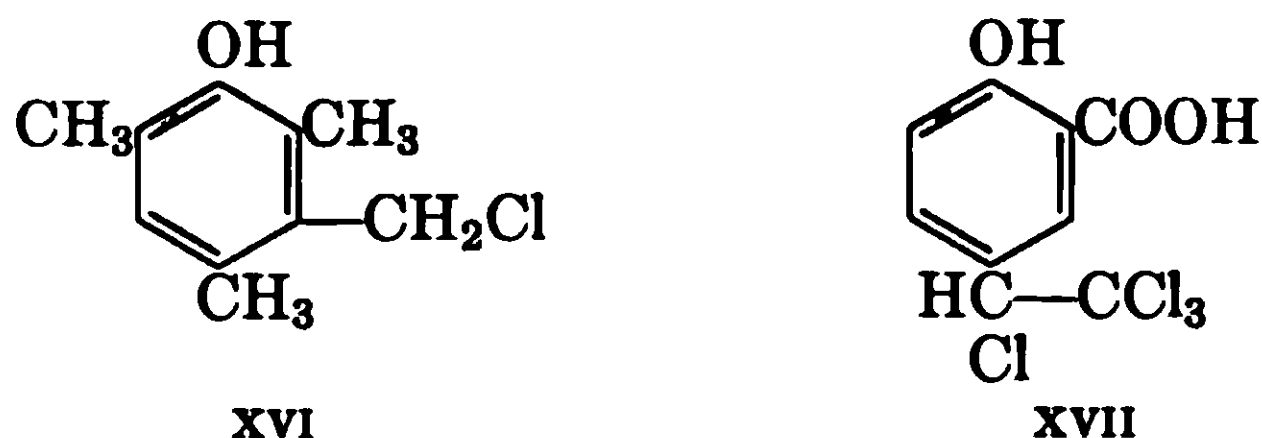
The slow addition of the phenol to a cooled solution containing an excess of formaldehyde, or its equivalent, saturated with the halogen acid tends to repress the formation of resin. By such a process the chloromethyl derivatives of *o*- and *p*-cresol, XIII and XIV, were pre-



pared.⁶⁰ Under similar conditions phenol gives the chloromethylated benzodioxan, XV.

Reaction ordinarily occurs at an *ortho* or *para* position of the phenol with the *para* position usually favored. When the *ortho* and *para* positions of the phenol are blocked the reaction may occur at the *meta* position.⁶¹ For example, the chloromethyl derivative of mesitol, XVI, has been prepared.

Chloroalkylation, analogous to chloromethylation, has been effected by the use of higher aldehydes in place of formaldehyde. Dharwarkar and Alimchandani⁶² obtained a chloroalkylated product, XVII, by reaction of salicylic acid with chloral in the presence of sulfuric acid and sodium chloride (which served as source of hydrogen chloride).

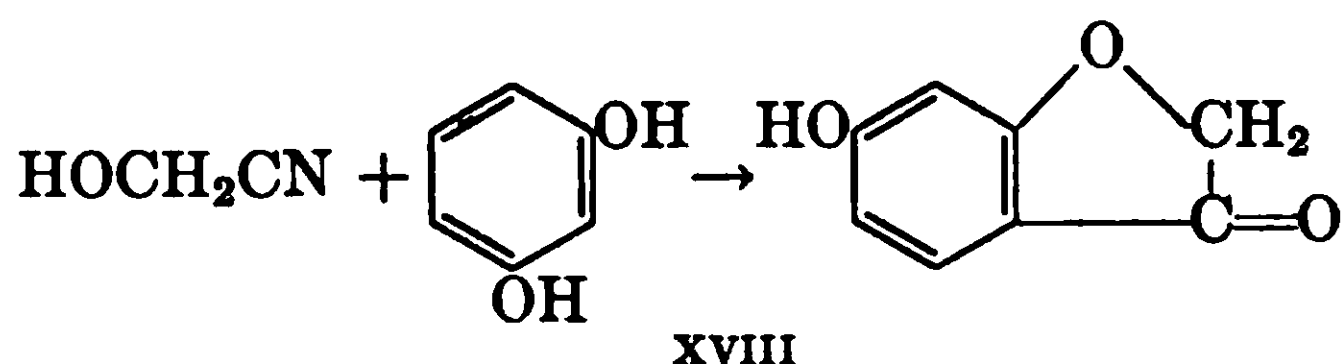


The use of hydrogen bromide in place of hydrogen chloride yields bromomethylphenols, but frequently the yields of the bromomethylphenol are lower than those of chloromethylphenol.^{56, 66}

CYANOMETHYLATION OF PHENOLS

A joint reaction between formaldehyde, a phenol, and an alkali metal cyanide analogous to the halomethylation or Mannich reaction was not found. However, phenolic-type Mannich bases have been reported to react with aqueous sodium cyanide to give a low yield of a hydroxyphenylacetic acid.¹² The acid apparently is derived by hydrolysis of an intermediate cyanomethylphenol. This reaction has received little attention.

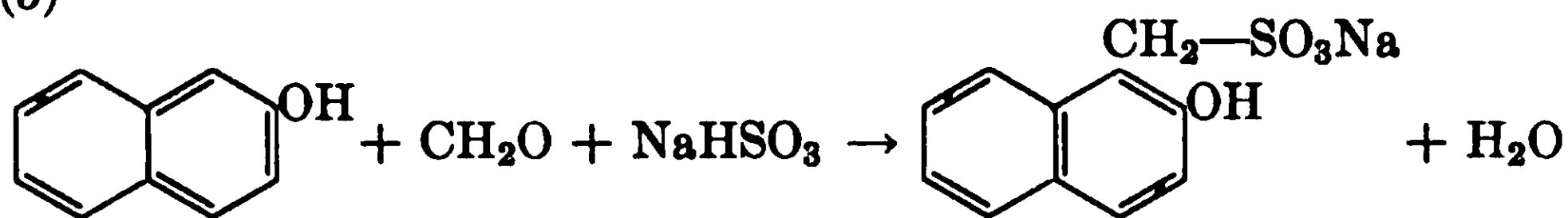
Methylene cyanohydrin, prepared from paraform and potassium cyanide, reacts with resorcinol in the presence of zinc chloride to give the cyclic ketone XVIII.⁶⁴



SULFOMETHYLATION OF PHENOLS

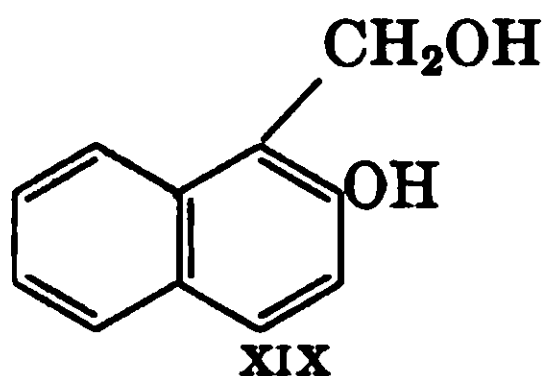
The sulfomethylation reaction, as applied to phenols, consists in the replacement of an *ortho* or *para* hydrogen atom of the phenol by an alkali metal sulfomethyl group, $-\text{CH}_2\text{SO}_3\text{M}$. The reaction was first accomplished by the joint reaction of β -naphthol, formaldehyde, and sodium bisulfite,⁶⁶ equation 5. The sulfomethylation of a variety of

(5)



phenols has been carried out, including α -naphthol, β -naphthol, 6-bromo-2-naphthol, *p*-cresol, 2,4-dimethylphenol, phenol, *p*-*tert*-butylphenol, saligenin, *p*-cresol monoalcohol, and dihydroxydiphenylsulfone,⁶⁵⁻⁶⁸ etc.

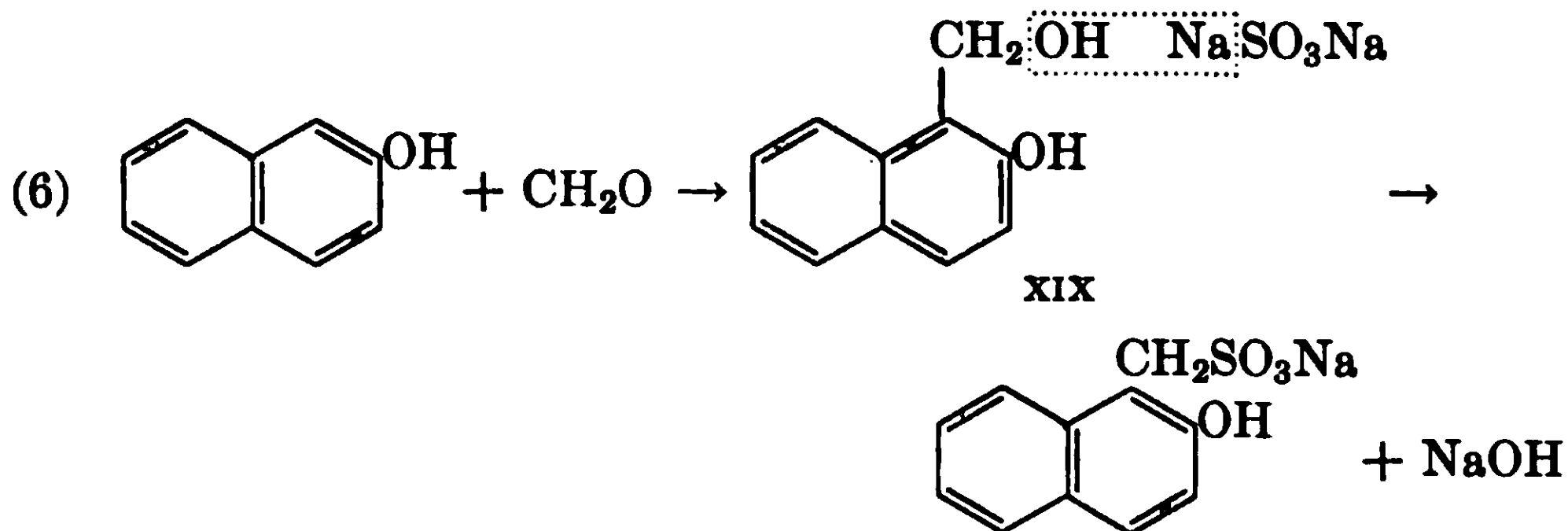
The reaction is ordinarily performed by the condensation of the phenol with aqueous formaldehyde and sodium bisulfite on a steam bath for several hours. With β -naphthol the yield of sulfomethylated product was around 75% of theory. When an equivalent amount of alkali is added to a 1:1:1 mixture of β -naphthol, formaldehyde, and sodium bisulfite, Suter, Bair, and Bordwell⁶⁶ found that the yield of sulfomethyl product dropped from 75% to 45% of theory and a 30% yield of α -hydroxymethyl β -naphthol, XIX, was formed.



Sulfomethylation will also occur with sodium sulfite, but the reaction is usually slower than with sodium bisulfite.⁶⁶ With sodium sulfite the yield is materially improved by increasing the mole ratio of sodium sulfite to phenol. For example, the yield of sulfomethyl derivative of *p*-cresol increased from 32% to 60–65% of theory on changing the ratio of *p*-cresol, formaldehyde, and sodium sulfite from 1:1:1 to 1:1:2.

In the sulfomethylation of phenol with formaldehyde and sodium sulfite, both mono- and disulfomethylated products were formed. However, difficulty was experienced in separation and purification of the products. When an attempt was made to condense β -naphthol with sodium sulfite and benzaldehyde, acetaldehyde, or acetone, essentially all the starting materials were recovered unchanged.⁶⁶ However, certain unsaturated ketones are reported to react with excess bisulfite and phenol.⁶⁹ Anisole failed to react with sodium sulfite and formaldehyde, indicating that the phenolic hydroxyl group is essential to reaction. The sulfomethyl derivatives of phenols are reasonably stable, although they may be condensed to give the methylene derivatives. The phenolic hydroxyl group may be etherified or esterified without destroying the products.

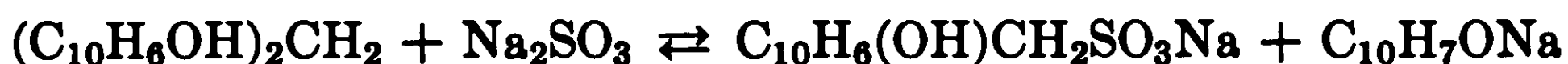
The mechanism of the sulfomethylation reaction, like that of the Mannich reaction, is not clear. Clutterbuck and Cohen⁷⁰ think that the reaction occurs as shown in equation 6. Suter, Bair, and Bord-



well have prepared compound XIX and found that it does not react with sodium sulfite under the conditions of the sulfomethylation reaction.⁶⁶ However, Shearing and Smiles⁶⁷ were unable to isolate XIX

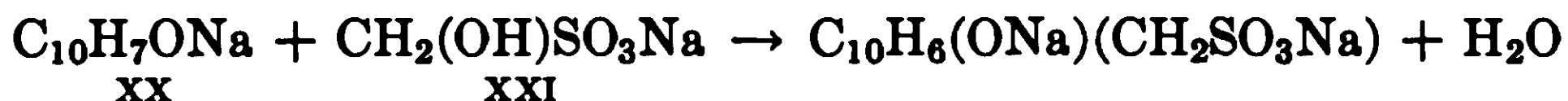
from reactions using β -naphthol. Their results with other phenols as well as with β -naphthol and formaldehyde and sodium sulfite are very interesting. Upon heating β -naphthol, formaldehyde, and sodium sulfite at 100°C. for 10 minutes a fairly good yield of di-2-hydroxy-naphthyl-1-methane was obtained. If the reaction was allowed to proceed for 3 hours the yield of the methylene derivative was very small, but the sulfomethylated product was obtained in good yields. These authors thus were able to separate the steps and show that the methylene derivative was first formed and then split by the sodium sulfite (equation 7).

(7)

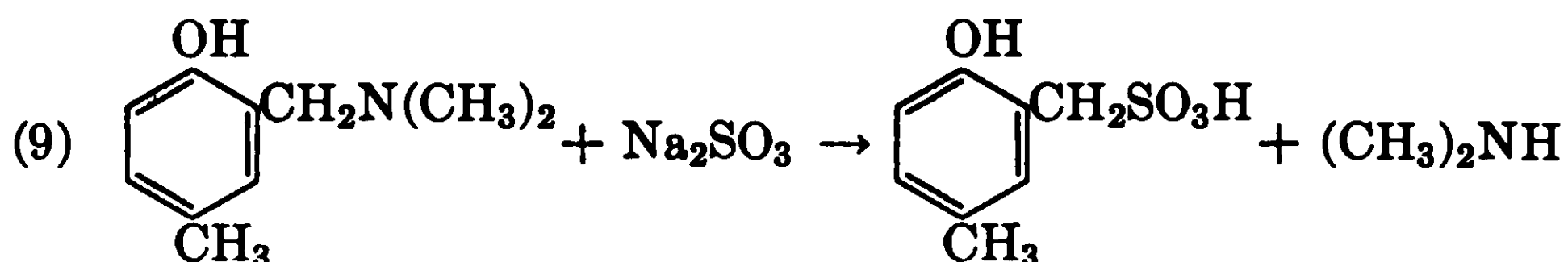


Quite surprisingly, saligenin and *p*-cresol monoalcohol both reacted with sodium sulfite to give a sulfomethylated product. It is also claimed that 3-methoxy-4-hydroxybenzyl alcohol and 3-methoxy-4-hydroxy- α -methylbenzyl alcohol react with aqueous bisulfite to give a sulfonate group in place of alcoholic hydroxyl group.⁷¹ It therefore appears that sulfomethylphenols may be obtained by three processes: (a) joint reaction of phenol with formaldehyde and sodium sulfite; (b) reaction of sodium sulfite with a methylene derivative of phenol; and (c) reaction of a phenol alcohol with sodium sulfite. In process (a), Shearing and Smiles consider that reaction occurs between the phenate XX and formaldehyde bisulfite XXI, equation 8.

(8)



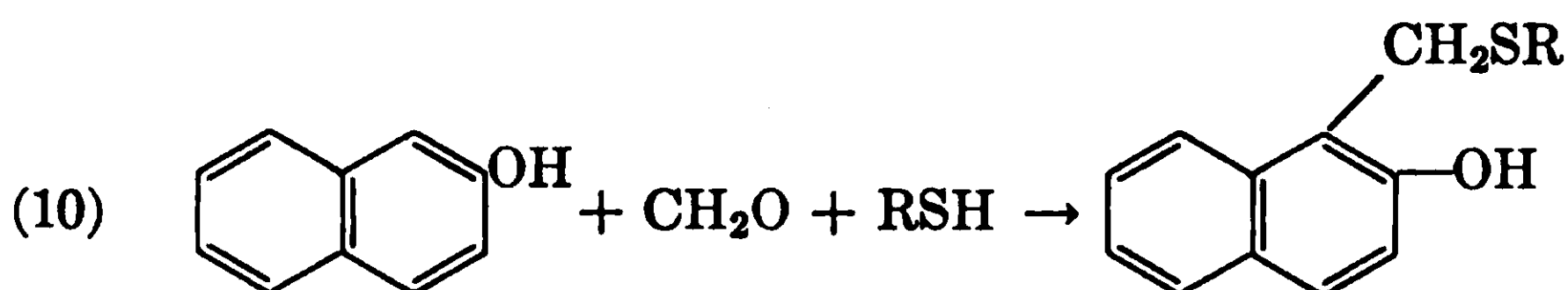
Erdtman⁷² has reported that phenolic-type Mannich bases react with aqueous sodium sulfite to give sulfomethylated phenols, equation 9. The sulfonate was isolated as a barium salt.



The sulfomethylated phenols may be used for the preparation of ion exchange resins⁷³ and tanning agents.⁷⁴ They have also been suggested for use as textile assistants⁶⁶ and as water-soluble resins.⁶⁶

ALKYLTHIAMETHYLATION OF PHENOLS

A reaction analogous to the Mannich reaction involving thiols, formaldehyde, and an active hydrogen compound has been reported by Pollelsdorf and Holt.⁷⁵ Indole, antipyrine, and β -naphthol were employed in the reactions. The reaction that occurred with β -naphthol is given, reaction 10. Yields of the β -naphthol derivative varied between 76% and 89% of theory. Ethyl, *n*-propyl, *n*-butyl, phenyl, and benzyl mercaptans were used in the reactions.



REFERENCES FOR CHAPTER 6

- ¹ H. Schafer and B. Tollens, *Ber.*, **39**, 2181 (1906).
- ² C. M. van Marle and B. Tollens, *Ber.*, **36**, 1351 (1903).
- ³ C. Mannich and E. Ganz, *Ber.*, **55**, 3486 (1922).
- ⁴ F. F. Blicke, *Organic Reactions*, Vol. 1, John Wiley & Sons, 1942, pp. 303-341.
- ⁵ J. F. Walker, *Formaldehyde*, Reinhold Publishing Corp., 1944, p. 172.
- ⁶ H. A. Bruson and G. W. MacMullen, *J. Am. Chem. Soc.*, **63**, 270-272 (1941).
- ⁷ H. A. Bruson, U. S. pat. 2,040,039 (1936).
- ⁸ A. L. Rawlins, W. F. Holcomb, E. M. Jones, F. H. Tendick, and J. H. Burckhalter, U. S. pat. 2,459,338 (1949).
- ⁹ J. H. Burckhalter, *J. Am. Chem. Soc.*, **72**, 6309-5310 (1950).
- ¹⁰ J. Decombe, *Comp. rend.*, **196**, 866-868 (1933).
- ¹¹ W. T. Caldwell and T. R. Thompson, *J. Am. Chem. Soc.*, **61**, 2354 (1939).
- ¹² E. L. Eliel, *J. Am. Chem. Soc.*, **73**, 43-45 (1951).
- ¹³ R. F. Brown and S. J. Miller, *J. Org. Chem.*, **11**, 388 (1946).
- ¹⁴ J. Decombe, *Comp. rend.*, **197**, 258-260 (1933).
- ¹⁵ W. Reeve and A. Saddle, *J. Am. Chem. Soc.*, **72**, 3252 (1950).
- ¹⁶ R. C. Carlin and H. R. Landerl, *J. Am. Chem. Soc.*, **72**, 2762-2763 (1950).
- ¹⁷ J. H. Burckhalter, *J. Am. Chem. Soc.*, **72**, 1308-1309 (1950).
- ¹⁸ A. H. Bruson, U. S. pat. 2,114,122 (1938).
- ¹⁹ A. Stempel and E. C. Buzzi, *J. Am. Chem. Soc.*, **71**, 2969-2972 (1949).
- ²⁰ K. S. Topchiev and V. I. Stavrovskaya, *Doklady Akad. Nauk S.S.S.R.*, **69**, 193-195 (1949).
- ²¹ A. P. Phillips, *J. Am. Chem. Soc.*, **73**, 3522-3523 (1951).
- ²² H. A. Bruson, *J. Am. Chem. Soc.*, **58**, 1741 (1936).
- ²³ J. B. Littman and W. R. Brode, *J. Am. Chem. Soc.*, **52**, 1655 (1930).
- ²⁴ V. I. Stavrovskaya and K. S. Topchiev, *Zhur. Obshchei Khim.*, **21**, 525-532 (1951).
- ²⁵ W. J. Moran, E. C. Schreiber, E. Engel, D. C. Behn, and J. L. Yamins, *J. Am. Chem. Soc.*, **74**, 127 (1952).

- ²⁶ H. Rapoport, T. P. King, and J. B. Lavinge, *J. Am. Chem. Soc.*, **73**, 2718 (1951).
- ²⁷ W. T. Caldwell and T. R. Thompson, *J. Am. Chem. Soc.*, **61**, 766-767 (1939).
- ²⁸ S. R. Finn and J. W. G. Musty, *J. Applied Chem.*, **1**, 182-184 (1951).
- ²⁸ S. R. Finn and J. W. G. Musty, *Chemistry & Industry*, **89**, 677 (1950).
- ³⁰ H. A. Bruson, U. S. pat. 2,265,141 (1942).
- ³¹ E. M. Jones, U. S. pat. 2,441,576 (1948).
- ³² K. Bodendorf and G. Koralewski, *Arch. Pharm.*, **271**, 101 (1933).
- ³³ S. V. Lieberman and E. C. Wagner, *J. Org. Chem.*, **14**, 1001 (1949).
- ³⁴ J. R. Feldman and E. C. Wagner, *J. Org. Chem.*, **7**, 31-47 (1942).
- ³⁵ E. R. Alexander and E. J. Underhill, *J. Am. Chem. Soc.*, **71**, 4014-4019 (1949).
- ³⁵ W. J. Burke et al., *J. Am. Chem. Soc.*, **71**, 609 (1949); **72**, 4691-4694 (1950); **74**, 602, 1518, 3601 (1952).
- ³⁷ M. Betti, *Gazz. chim. ital.*, **331**, 5 (1903).
- ³⁸ H. R. Snyder and J. H. Brewster, *J. Am. Chem. Soc.*, **70**, 4230 (1948).
- ³⁹ A. C. Zettlemeyer and D. M. Wace, *Ind. Eng. Chem.*, **42**, 491-495 (1950).
- ⁴⁰ Rohm and Haas Company, *Tech. Bull.*, "Dimethylaminomethyl Phenols."
- ⁴¹ Grassi and Maselli, *Gazz. chim. ital.*, **28**, II, 477 (1898).
- ⁴² R. Stoermer and K. Behn, *Ber.*, **34**, 2455 (1901).
- ⁴³ C. A. Buehler, R. L. Brown, J. M. Holbert, J. G. Fulmer, and G. W. Parker, *J. Org. Chem.*, **6**, 902-907 (1941).
- ⁴⁴ C. A. Buehler, F. Deebel, and R. Evans, *J. Org. Chem.*, **8**, 216-219 (1941).
- ⁴⁵ S. Van der Meer, *Rubber Chem. and Technol.*, **18**, 853-873 (1945).
- ⁴⁶ R. C. Fuson and C. H. McKeever, *Organic Reactions*, Vol. I, John Wiley & Sons, pp. 63-91.
- ⁴⁷ Ger. pat. 132,475 (1900).
- ⁴⁸ I. G. Farbenindustrie, Ger. pat. 494,803 (1930).
- ⁴⁹ C. A. Buehler, B. C. Bass, R. B. Darling, and M. E. Lubs, *J. Am. Chem. Soc.*, **62**, 890 (1940).
- ⁵⁰ C. A. Buehler, G. F. Deebel, and R. Evans, *J. Org. Chem.*, **6**, 216 (1941).
- ⁵¹ C. A. Buehler, F. K. Kirchner, and G. F. Deebel, *Org. Syntheses*, **20**, 59 (1940).
- ⁵² F. Bayer and Company, Ger. pat. 113,723 (1900).
- ⁵³ Ger. pat. 114,494 (1900).
- ⁵⁴ S. Van der Meer, *Paper 47*, Rubber-Stichting, Delft, Holland, 1944.
- ⁵⁵ S. Van der Meer, *Paper 48*, Rubber-Stichting, Delft, Holland, 1944.
- ⁵⁶ Murahashi and Matsukawa, *Bull. Inst. Phys. Chem. Research Tokyo*, **21**, 509-519 (1942).
- ⁵⁷ C. A. Buehler, *Tenn. Acad. Sci.*, **22**, 303-310 (1947).
- ⁵⁸ R. Trave, *Gazz. chim. ital.*, **80**, 502-509 (1950).
- ⁵⁹ H. Einhorn, *Ann.*, **348**, 244-245 (1905).
- ⁶⁰ I. G. Farbenindustrie, French pat. 695,602 (1930); Brit. pat. 347,887 (1931).
- ⁶¹ S. R. Finn and J. W. G. Musty, *J. Soc. Chem. Ind.*, Suppl. Issue, No. 1, S3-S7 (1950).
- ⁶² H. V. Dharwarkar and R. L. Alimchandani, *J. Indian Chem. Soc.*, **17**, 416-421 (1940).
- ⁶³ W. M. Bright and P. Cammarata, *J. Am. Chem. Soc.*, **74**, 3690 (1951).
- ⁶⁴ W. K. Slater and H. Stephen, *J. Chem. Soc.*, (1), 117, 309-318 (1920).
- ⁶⁵ F. Bayer and Company, Ger. pat. 87,335 (1896).

- ⁶⁶ C. M. Suter, R. K. Bair, and F. G. Bordwell, *J. Org. Chem.*, **10**, 470-478 (1945).
- ⁶⁷ E. A. Shearing and S. Smiles, *J. Chem. Soc.*, **1937**, 1348-1357.
- ⁶⁸ Kuhlmann, French pat. 853,940 (1940).
- ⁶⁹ F. Becherer, U. S. pat. 2,212,224 (1941).
- ⁷⁰ F. W. Clutterbuck and J. B. Cohen, *J. Chem. Soc.*, **1923**, 2507-2515.
- ⁷¹ B. O. Lindgren, *Acta Chem. Scand.*, **3**, 1011-1020 (1949); **4**, 1305-1374 (1950).
- ⁷² H. G. H. Erdtman, Swed. pat. 130,523 (1951).
- ⁷³ H. M. Day and R. L. DeHoff, U. S. pat. 2,522,509 (1950).
- ⁷⁴ H. Noerr, G. Mauthe, R. Bauer, H. Schütte, and F. W. Guthke, Ger. pat. 696,581 (1940).
- ⁷⁵ F. Poppelsdorf and S. J. Holt, *J. Chem. Soc.*, **1954**, 1124-1130.

C H A P T E R S E V E N

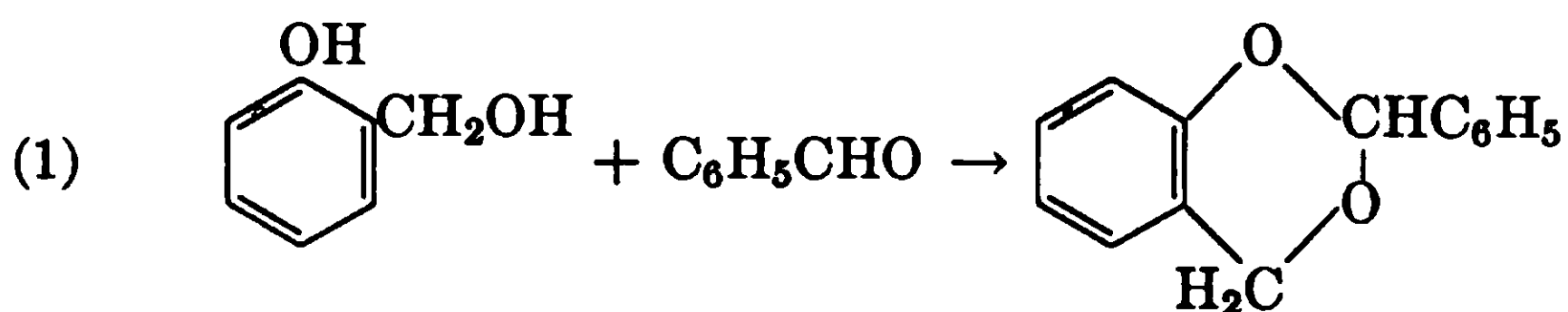
Heterocyclic Products

A variety of ring compounds may be prepared by the direct reaction of phenols with an aldehyde or ketone. It is also possible, in certain instances, to prepare the phenol-aldehyde or ketone condensation product and treat these products with a third reagent to form the cyclic product. The new ring compounds contain a five- or six-membered heterocyclic ring attached at the 1,2-positions to the aromatic ring of the phenol. The more important ring compounds where oxygen is the hetero atom in the ring are the benzodioxans, benzofurans, coumarins, chromones, chromans, xanthenes, benzopyrilium and xanthopyrilium salts, and certain miscellaneous compounds. Dihydrocoumarazones, dihydrobenzoxazones, and the dihydrobenzoxazines, all of which have nitrogen in the heterocyclic ring, may also be formed. Only a limited number of compounds which have sulfur in the heterocyclic ring have been reported.

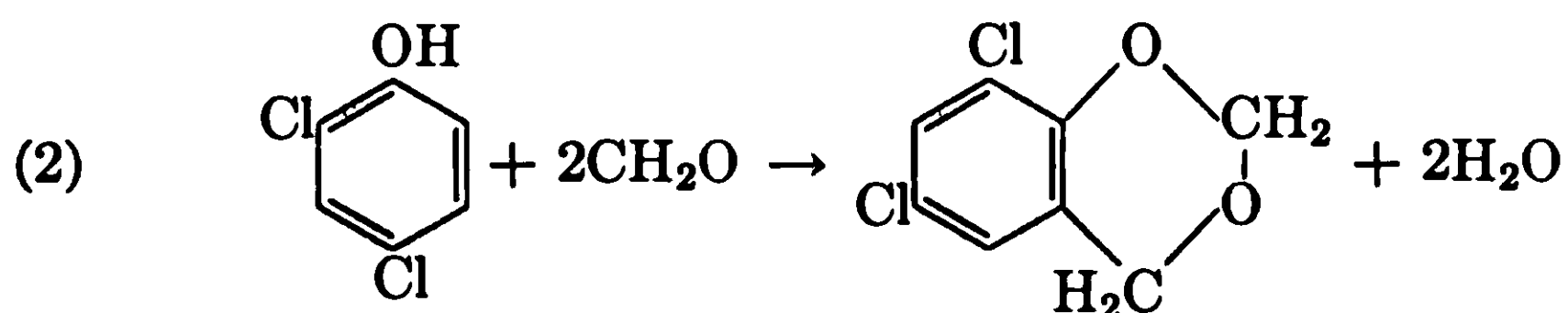
A. HETEROCYCLIC COMPOUNDS WITH OXYGEN IN RING

Benzodioxans

One of the most common classes of cyclic compounds formed by the condensation of phenols and aldehydes are the benzodioxans. Inspection of the structural formula of a benzodioxan indicates that they are cyclic acetals formed by reaction of both the phenolic and alcoholic hydroxyl groups of an *ortho*-hydroxybenzyl alcohol with an aldehyde. The validity of such a conclusion is borne out by the fact that the compounds may be prepared from an *ortho*-hydroxybenzyl alco-

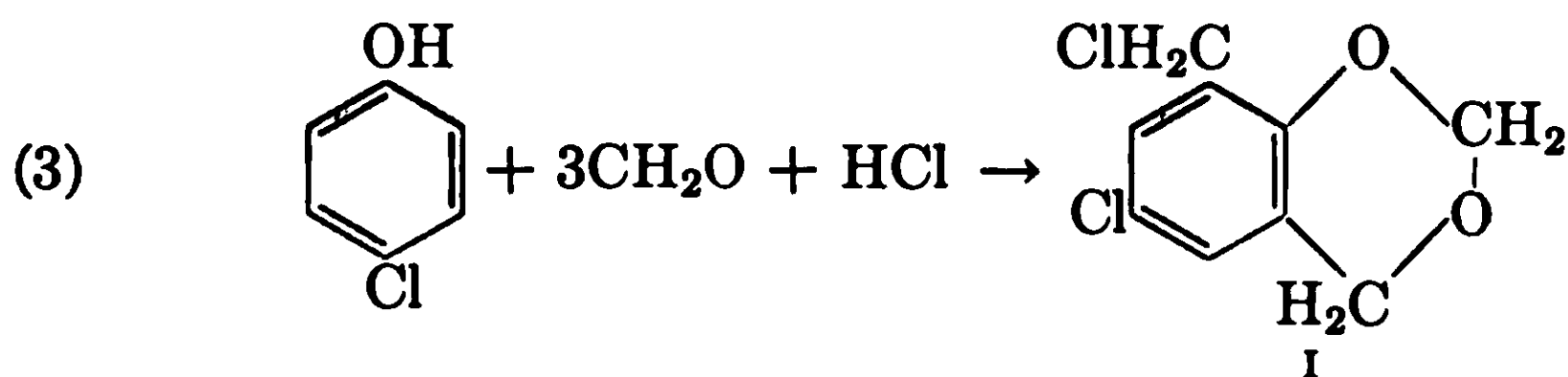


hol and an aldehyde, equation 1. The reverse reaction, hydrolysis of a benzodioxan to phenol alcohol and an aldehyde, is also possible with some benzodioxans. The usual procedure for the preparation of a benzodioxan is by the direct reaction of a phenol with an excess of an aldehyde, equation 2.

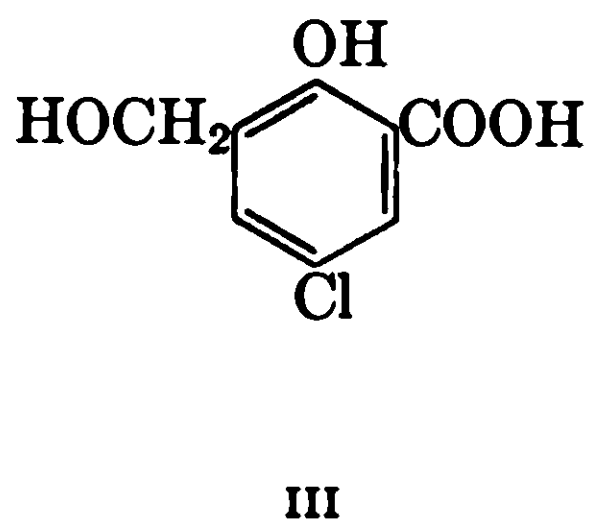
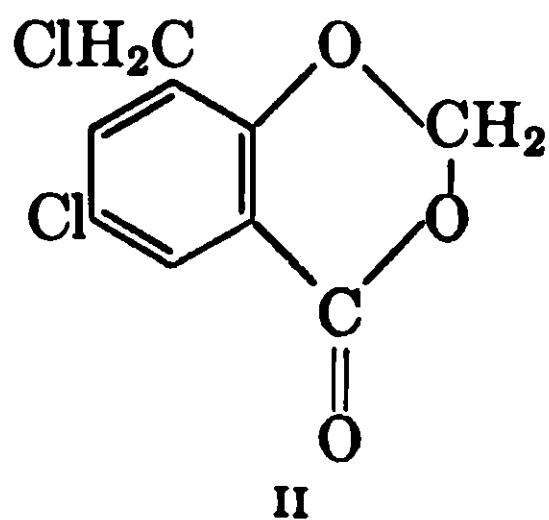


Where a phenol alcohol is the starting material at least one of the methylol groups must be *ortho* to the phenolic hydroxyl group. This is required in order that ring closure may occur upon reaction with the aldehyde. If a phenol is used in place of the phenol alcohol, the phenol must be selected so that reaction may occur at an *ortho* position. For this reason the *para*-substituted phenols are preferred. Because of less tendency to form resin, phenols carrying negative or halogen substituents give the highest yields of benzodioxans. Numerous phenols and phenol alcohols have been used in the synthesis.¹⁻²⁶ Formaldehyde, chloral, benzaldehyde, and acetaldehyde have been the aldehydes most commonly employed.

Mineral acids, often at high concentrations, are employed as catalysts. When halogen acids are used with phenols having more than one position available for reaction, halomethylation may accompany the formation of the benzodioxan,^{7,14,16,27} equation 3. The structure

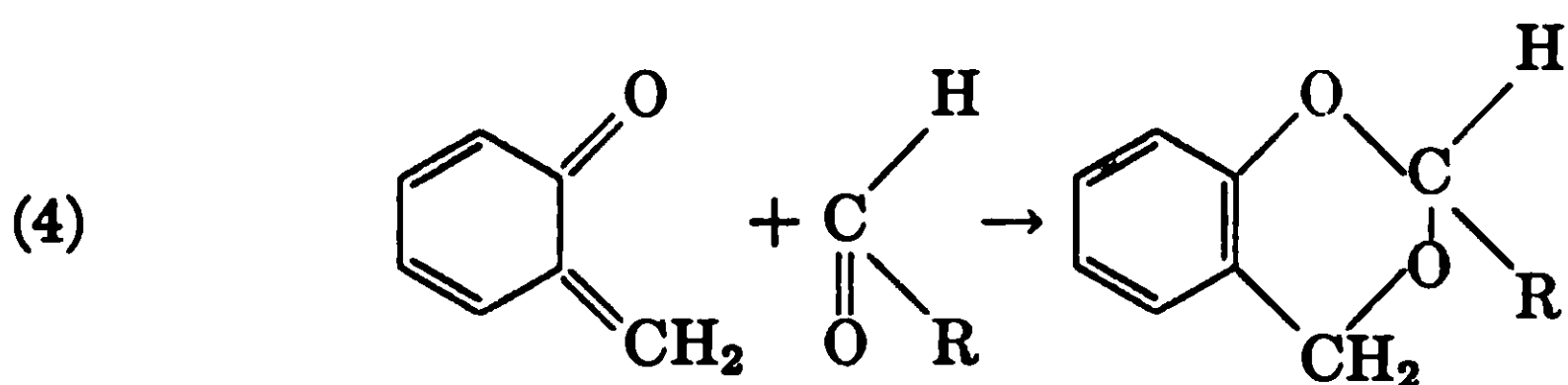


of the benzodioxan, I, was shown by oxidation of I to the carbonyl compound II according to the method of Borsche and Berkhout,¹ followed by hydrolysis of II to the acid, III. Sulfuric acid is the most

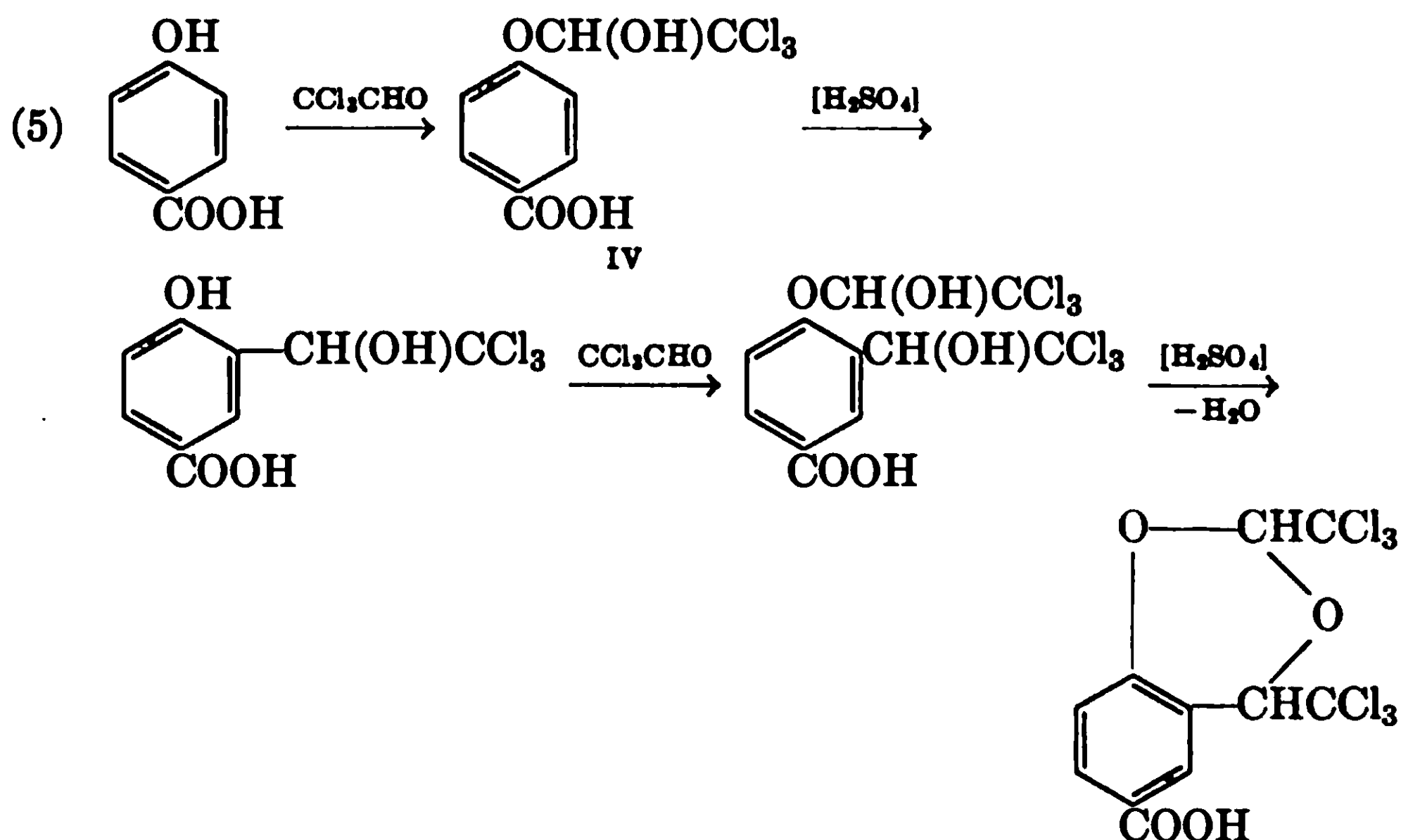


useful catalyst with the less reactive phenols, such as the nitro and carboxy phenols.^{2-4,6} Benzoic acid is one of few organic acids which have been employed as catalyst. It was used to promote the condensation of saligenin with benzaldehyde, 2-phenylbenzodioxan-1,3, resulting.²⁸

Hultzs²⁸ thinks that the benzodioxans are formed by the addition of a quinone methide, resulting from dehydration of the phenol alcohol, to the unsaturated carbonyl group of the aldehyde, equation 4. There is little experimental evidence for this mechanism. Chattaway^{2,8} has pictured the formation of an intermediate hemiacetal, IV.

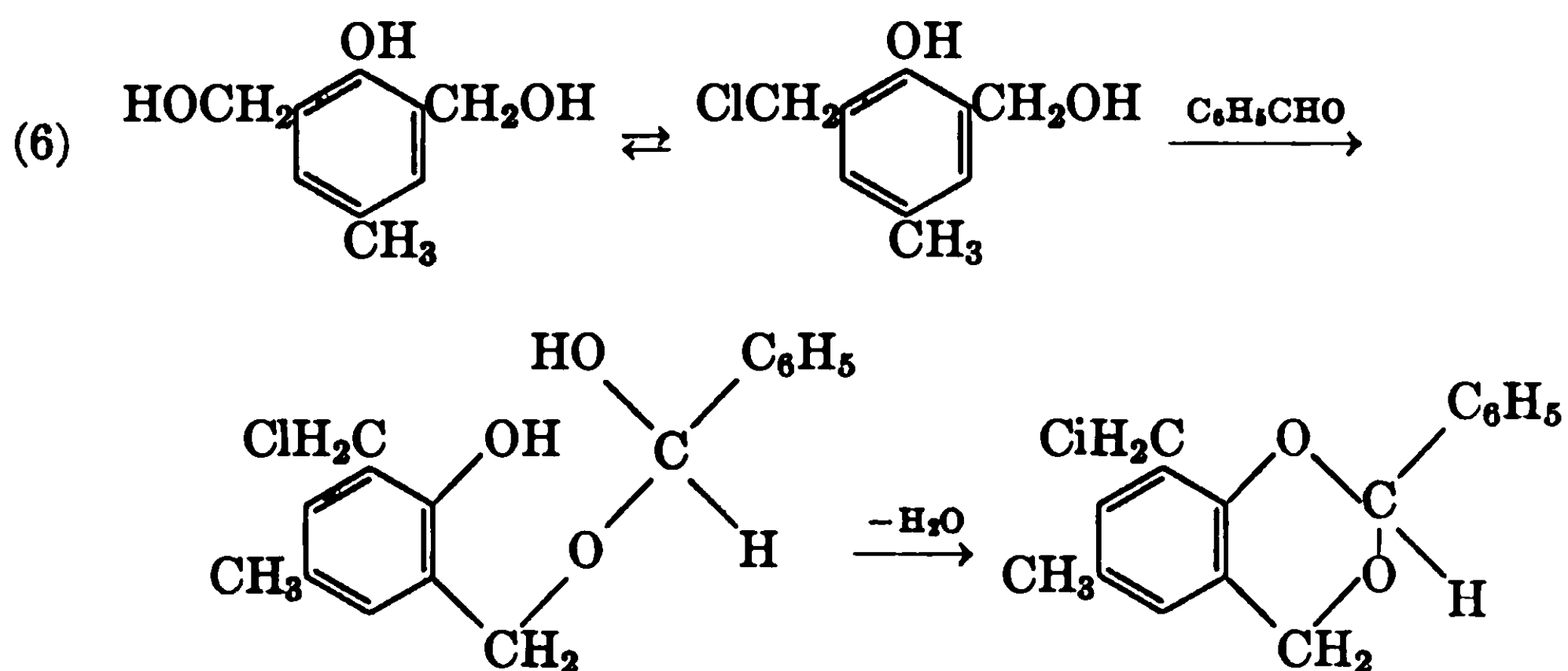


The steps in the reaction of *p*-hydroxybenzoic acid with chloral, as visualized by Chattaway,⁸ are shown in equation 5. The intermediate hemiacetal, IV, may be isolated when chloral is used.³⁰

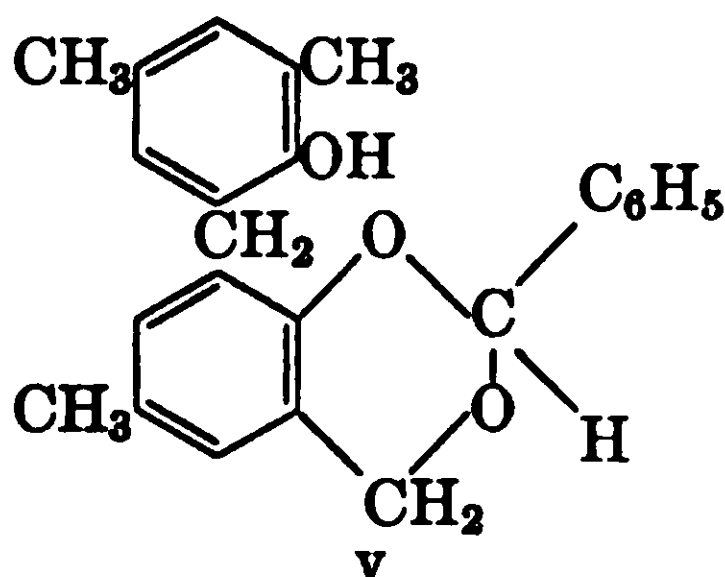


Ziegler and coworkers^{14,16} reacted *p*-cresol dialcohol with benzaldehyde in the presence of concentrated hydrochloric acid. They pictured the reaction as occurring by formation of the chloromethyl derivative, which then reacted with benzaldehyde to form the benzo-

dioxan with a hemiacetal involving the methylol group rather than the phenolic hydroxyl group acting as the unstable intermediate, equation

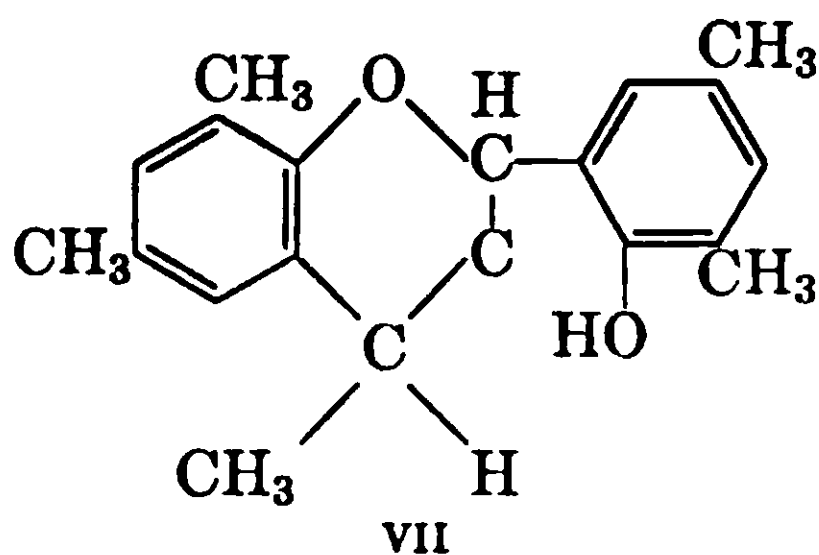
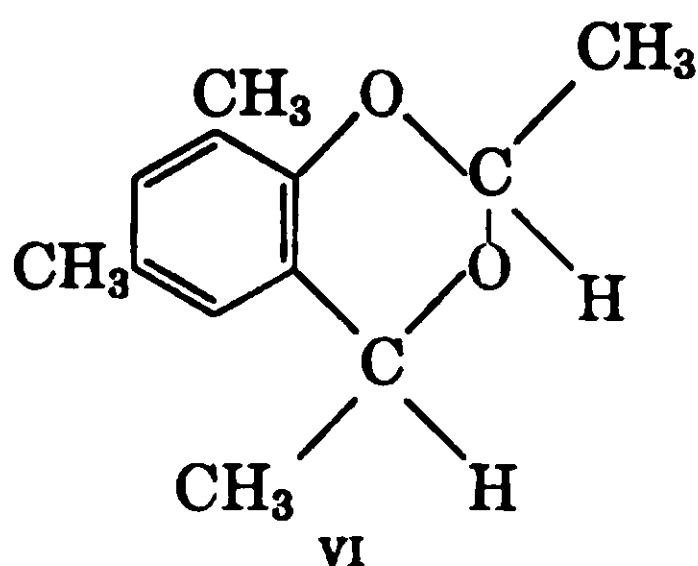


6. If this reaction is conducted in the presence of 2,4-dimethylphenol the hydroxybenzyl-substituted benzodioxan V is formed. Thiocyno-

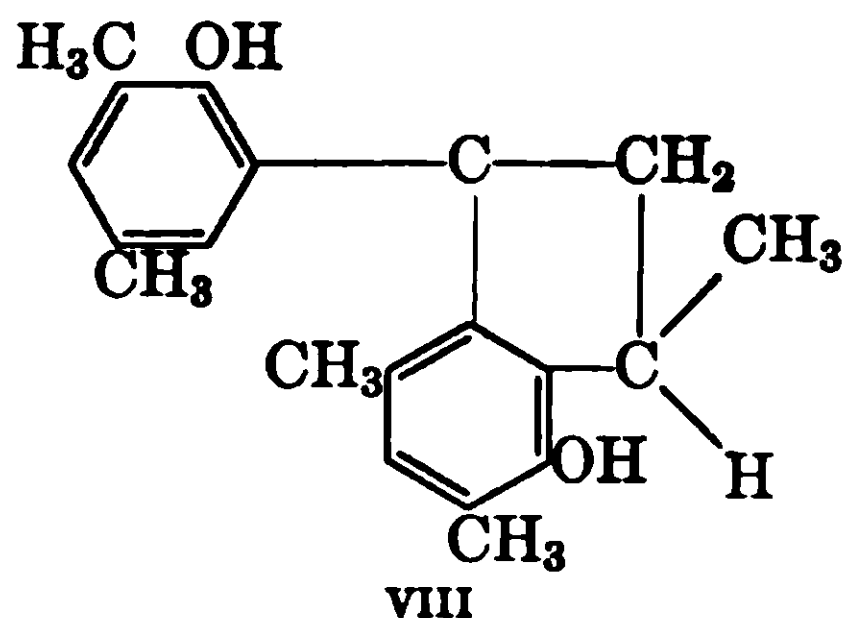


methyl-*p*-cresol monoalcohol behaved like the chloromethyl derivative of *p*-cresol monoalcohol in that it also gave a benzodioxan.¹⁷

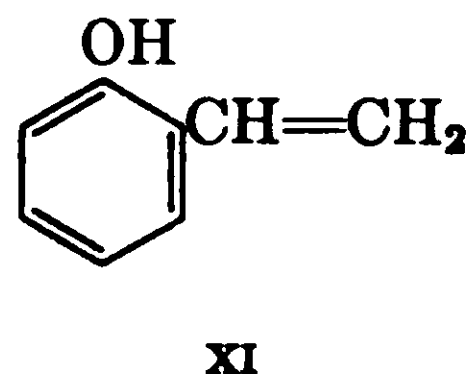
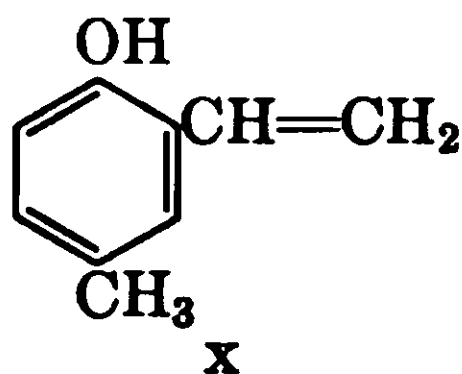
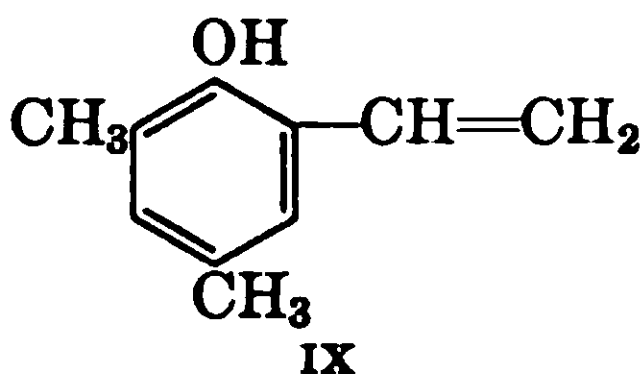
Adler²² and coworkers prepared the benzodioxan VI by reaction of 2,4-dimethylphenol with an excess of acetaldehyde. On attempted fission of the compound with acids and alkalies, a chroman, VII, was obtained along with a small amount of a compound which was as-



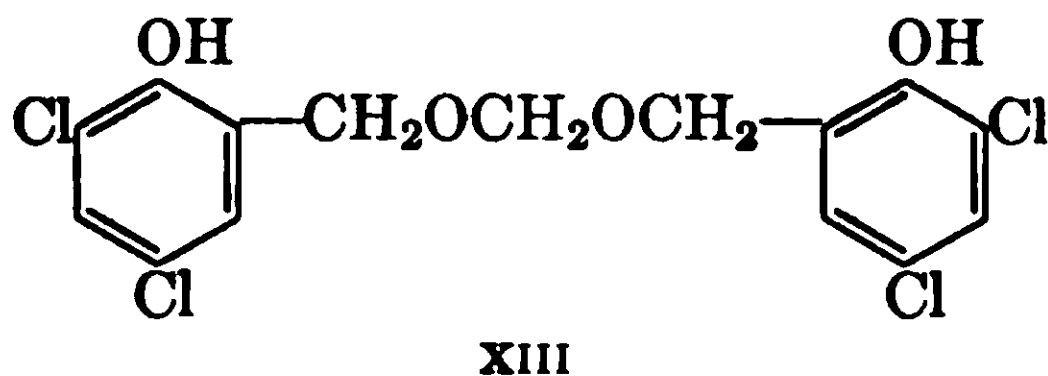
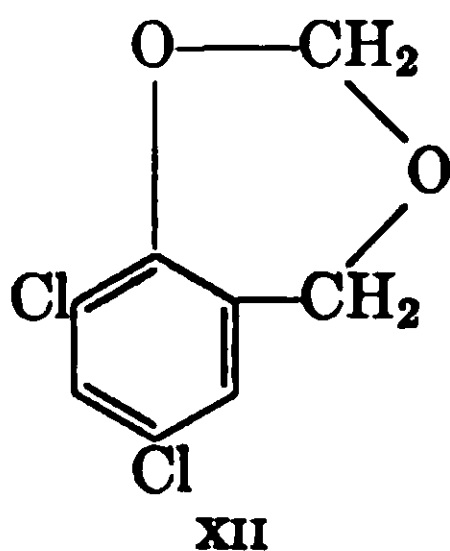
signed structure VIII. When the benzodioxan was heated over Frankonite at 400–650°C. monomeric vinyl phenols were obtained in excel-



lent yield. The vinyl phenols IX, X, XI were prepared in this manner from the appropriate benzodioxans.

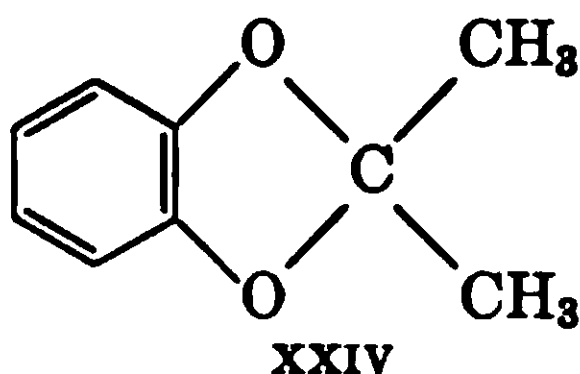


Ziegler, Meralla, and Simmler^{12,13} made a detailed study of the reaction of 2,4-dichlorophenol with trioxymethylene using sulfuric acid as catalyst. Besides the dihydroxydiphenylmethane, they obtained the benzodioxan, XII, and the linear acetal, XIII. The two com-



pounds could be converted from one to the other under proper conditions. The authors pictured the transformation as occurring by formation of 2,4-dichlorophenol monoalcohol as an intermediate. The isolation of XIII and similar substituted dibenzyl formals starting with other phenols suggests that such acetals may play a far more important role in the reaction of phenols with aldehydes than has been generally assumed.

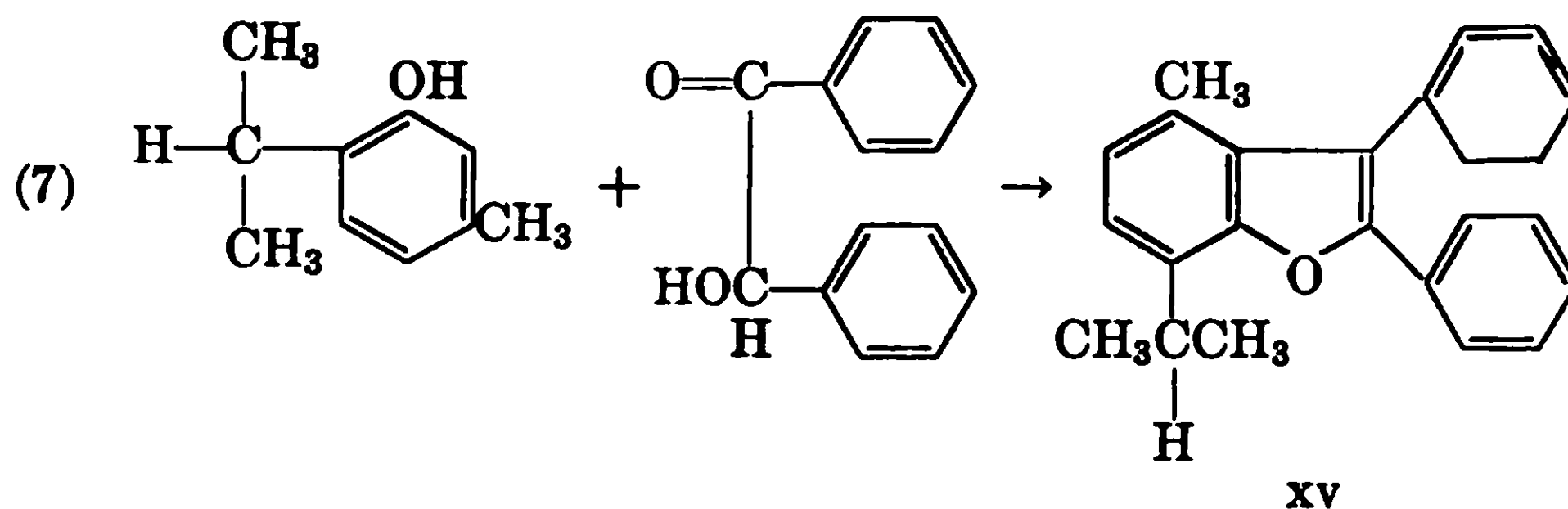
An interesting cyclic acetal, XXIV, has been obtained by Sloof³¹ by the condensation of acetone with catechol. Kohn³² has verified the structure proposed by Sloof.



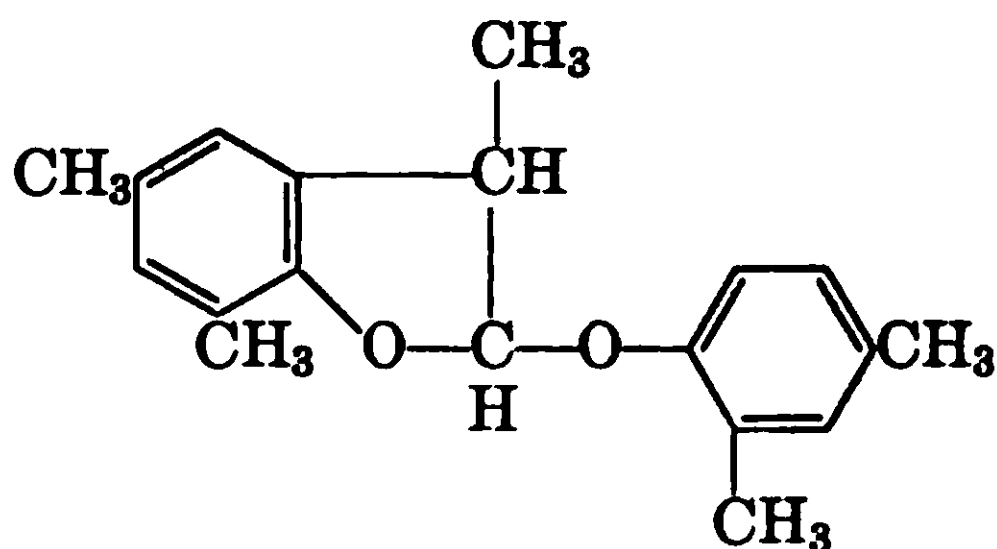
Benzofurans

The benzofurans are an interesting class of compounds whose chemistry has been reviewed by Elderfield and Meyer.³³ A number of methods are available for the preparation of such compounds, but only those involving the direct condensation of phenols with aldehydes or ketones will be considered here. It will be noted from a review of the literature that only a very limited number of aldehydes or ketones have been useful in such syntheses. A primary requirement of the aldehyde or ketone is that it contain a second functional group, e.g. double bond, hydroxyl group or a second carbonyl group. If the carbonyl compound does not possess a second functional group it must then be capable of forming one during reaction.

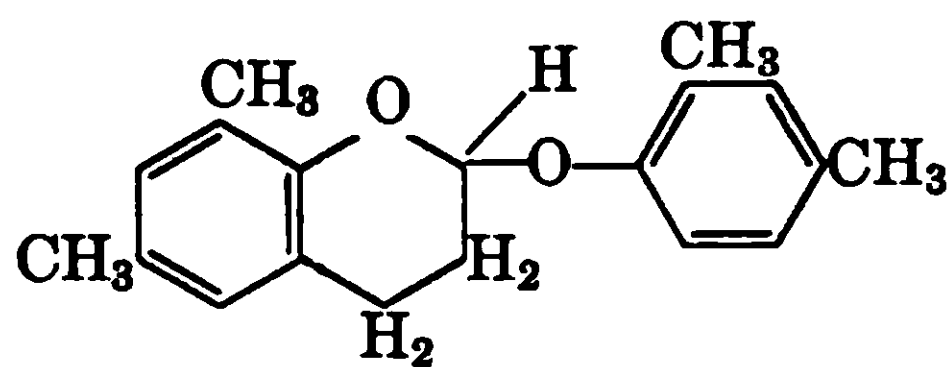
Benzoin reacts with thymol in the presence of 73% sulfuric acid to form a 2,3-diphenylbenzofuran, equation 7. A similar reaction occurs with benzoin and hydroquinone.³⁴



According to Adler³⁵ acrolein reacts with 2,4-dimethylphenol to give a dihydrobenzofuran, XVI. Clayton and coworkers³⁶ object to the structure assigned by Adler and propose the chroman structure XVII as being in better agreement with the chemical and physical properties of the compound.

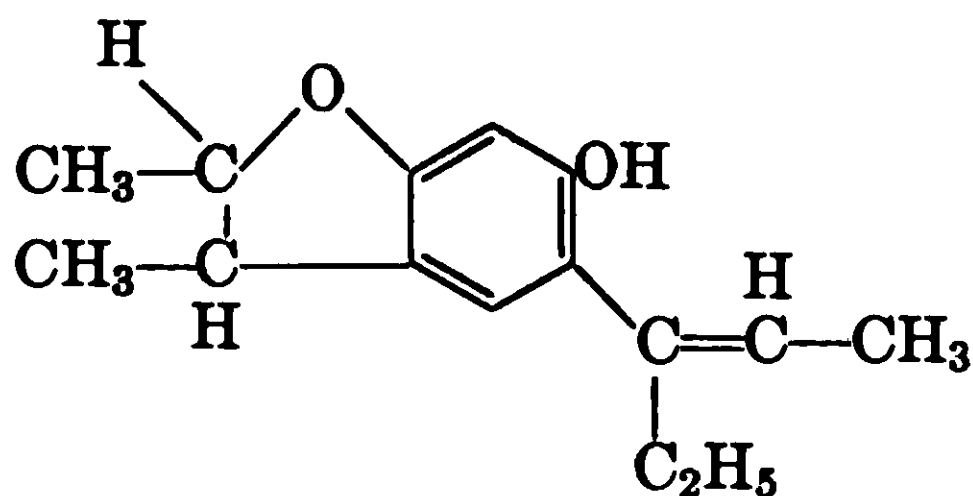


XVI

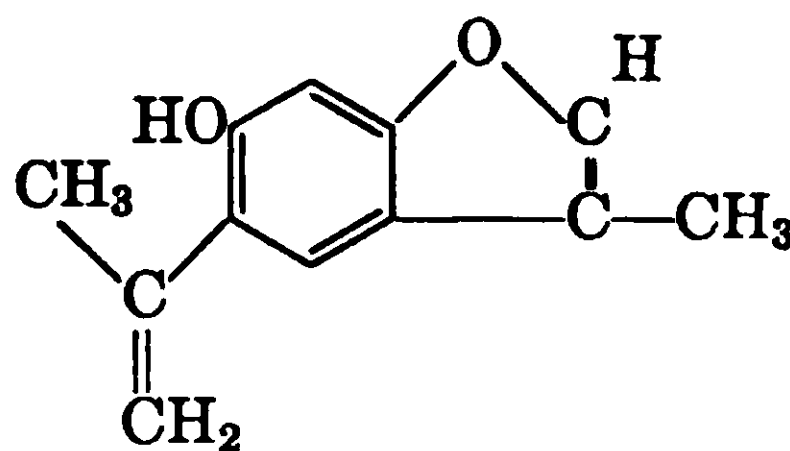


XVII

When resorcinol was condensed with diethyl ketone in glacial acetic acid using dry hydrogen chloride as catalyst, Niederl and Niederl³⁷ observed a simultaneous alkylation of the phenol and ring formation. The product was assigned structure XVIII. Under similar reaction



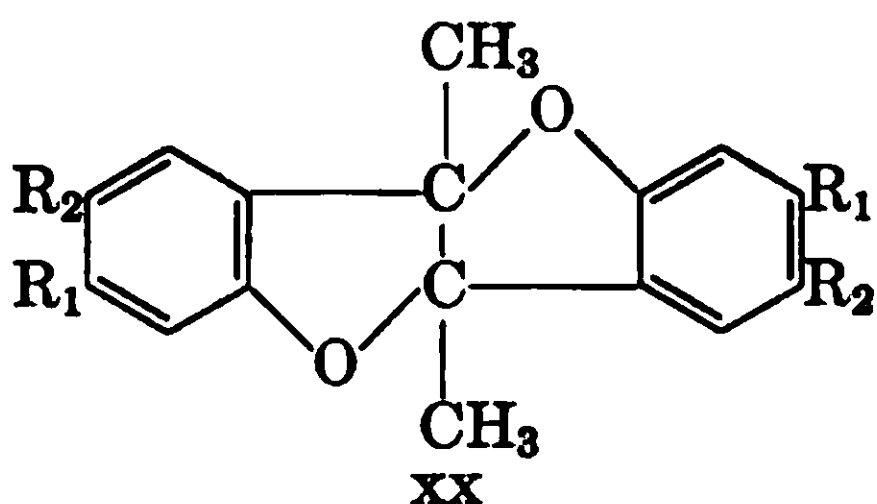
XVIII



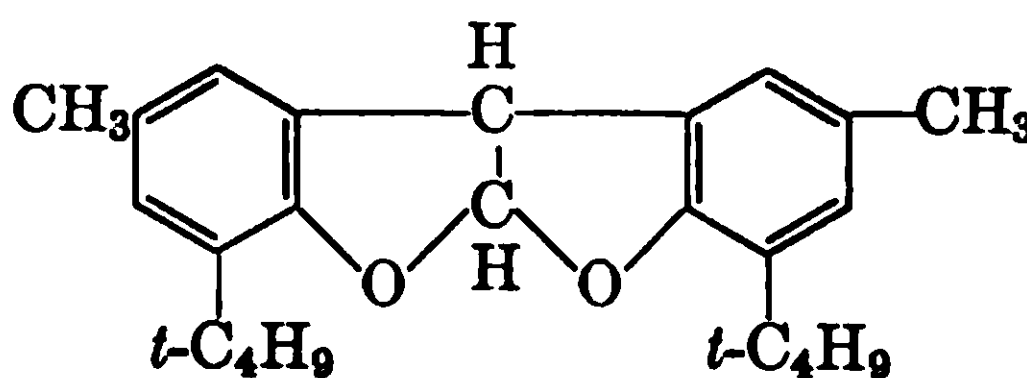
XIX

conditions acetone formed a benzofuran XIX instead of a dihydrobenzofuran such as was obtained with diethyl ketone.

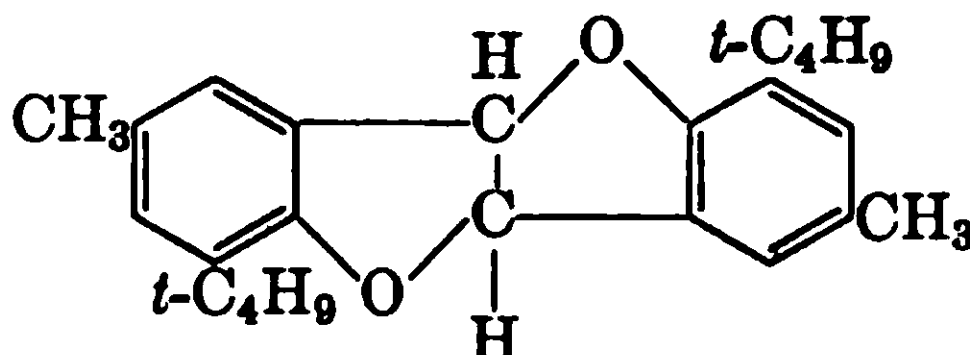
Biacetyl has been condensed with various phenols to give multiple ring compounds, such as XX, which logically may be considered along with benzofurans.³⁸ As might be expected, similar products may be



XX



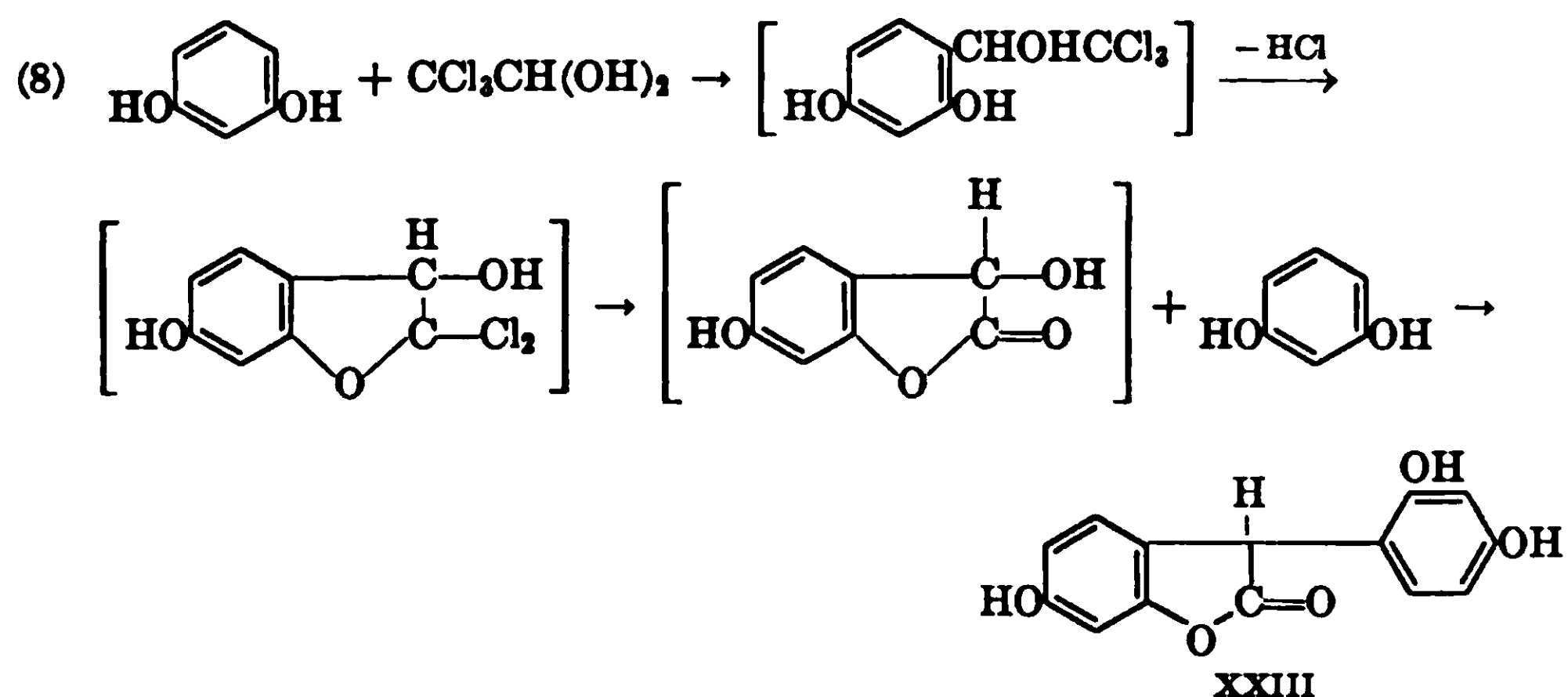
XXI



XXII

obtained with glyoxal.³⁹ From the experimental data available the authors were unable to decide between structures XXI and XXII for the product from glyoxal and *o*-*t*-butyl-*p*-cresol.

One of the earliest procedures for the preparation of a benzofuranone was discovered by Hewitt and Pope,⁴⁰ who found that certain phenols react with aldehydes such as chloral hydrate to give a benzofuranone, XXIII, substituted in the 3-position. The reaction is carried out by heating the reactants to around 100°C. in the presence of potassium acid sulfate. The scheme proposed for the reaction between resorcinol and chloral hydrate is shown in equation 8.



Coumarins

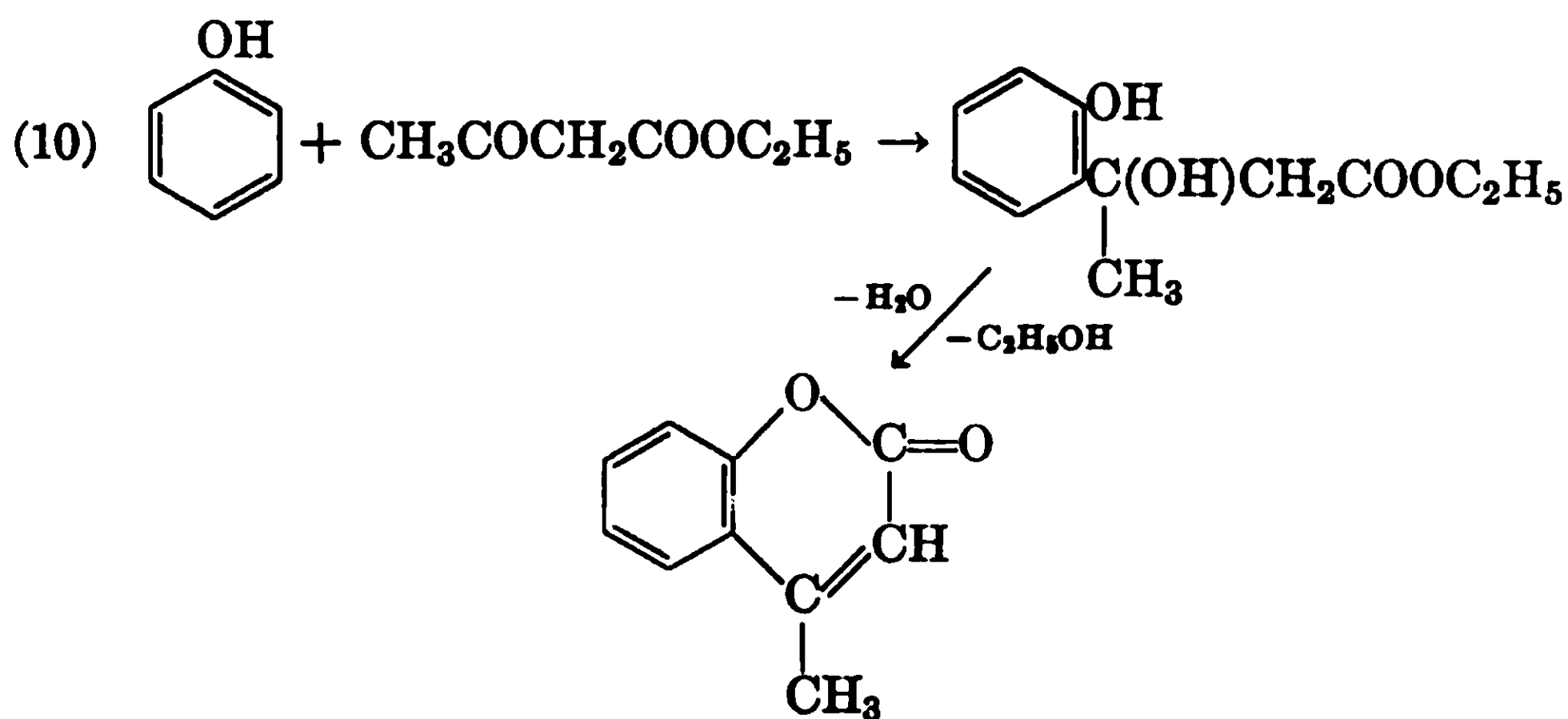
The von Pechmann reaction, which involves the condensation of malic acid or a β -keto ester with the proper phenol, is most frequently used for the preparation of coumarins.⁴¹⁻⁴⁷ We are concerned here only with reactions where a β -keto ester is employed, equation 9.



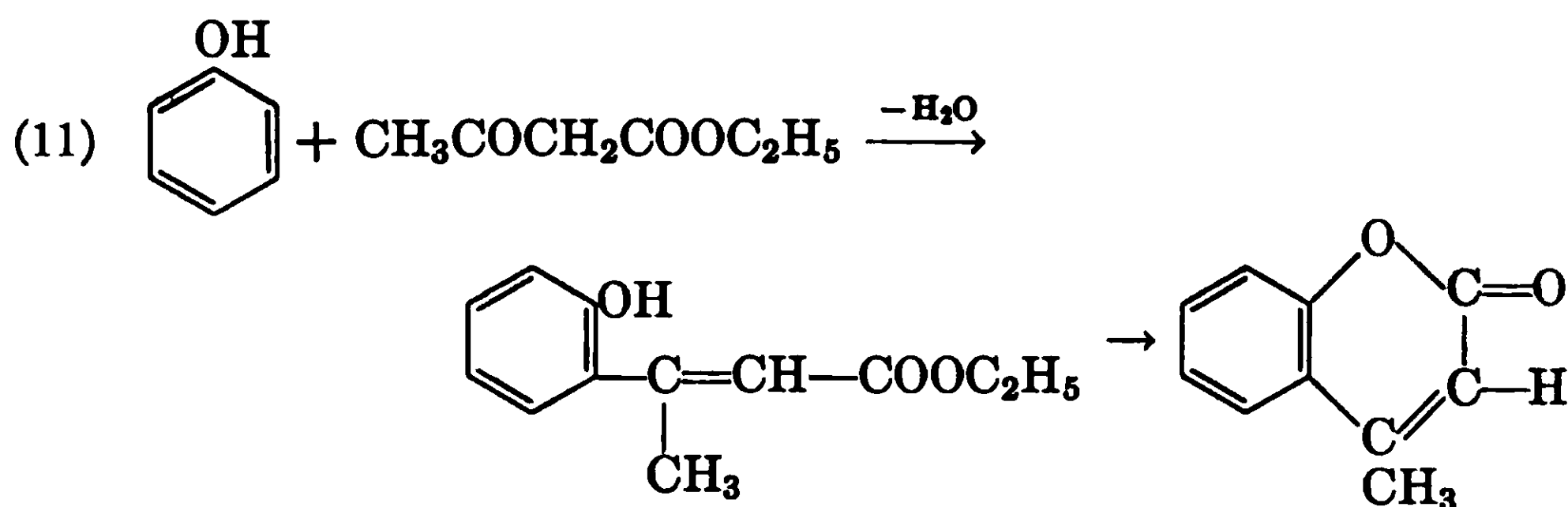
Sulfuric acid (preferably 73%) is a common catalyst for the reaction, but numerous other catalysts such as hydrogen chloride, zinc chloride, boric anhydride, phosphorus pentoxide, and sodium acetate have been used. The ease with which the reaction takes place is affected not only by the type of phenol and the keto ester but also by the choice

of catalyst. In general, phenols with *ortho-para* directing groups particularly when substituted at the *meta* position are more reactive than phenols with negative groups.⁴⁸⁻⁵² Besides acetoacetic esters, other keto esters also may be used in the reaction.⁵³⁻⁵⁶ The activity of alkyl-substituted esters drops off as the size of the alkyl substituent is increased, although acetone dicarboxylic acid is nearly as active as acetoacetic esters.⁵⁷

Two mechanisms have been suggested for the reaction.^{41, 42, 58, 59} The formation of an intermediate hydroxy compound, actually a substituted phenol alcohol, has been proposed. Ring closure might then result by elimination of a molecule of water and a molecule of alcohol from the intermediate hydroxy compound, reaction 10. On the other



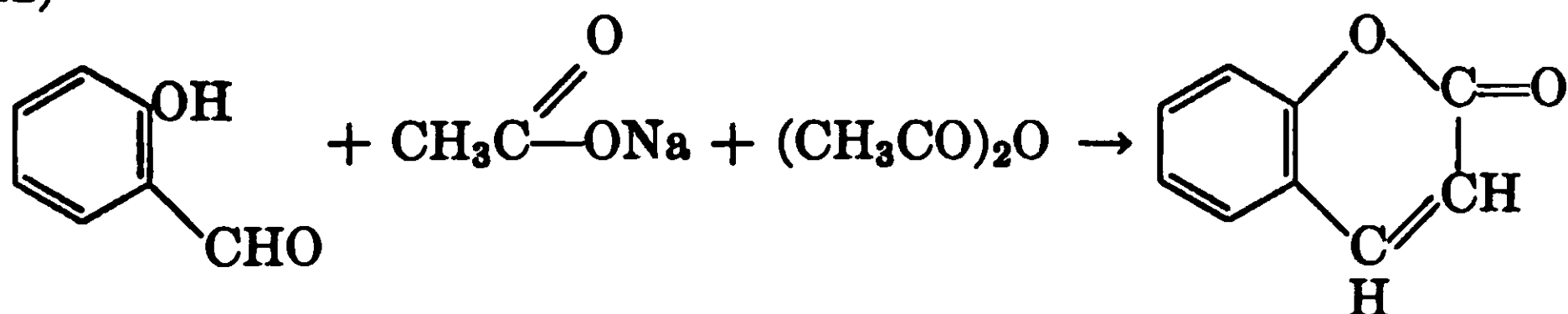
hand a cinnamic acid ester may be the active intermediate, reaction 11.



In support of that mechanism it has been shown that certain cinnamate esters may be converted to coumarins by the action of sulfuric acid, a common catalyst for the von Pechmann reaction. So far conclusive evidence for either mechanism is lacking.

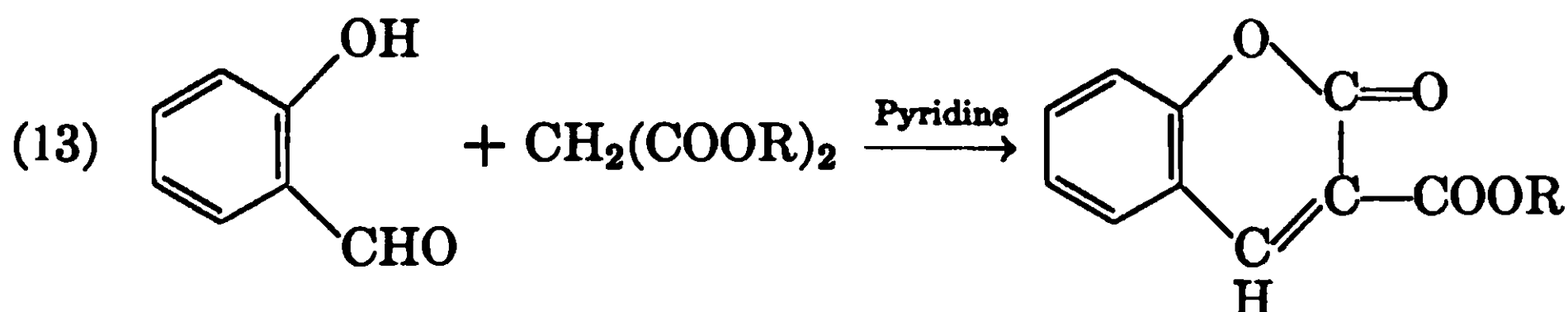
Coumarins also may be obtained by means of the Perkin reaction starting with an ortho hydroxybenzaldehyde, equation 12. The yields

(12)



vary widely in this reaction but often are only fair or poor owing to the resinification of the phenolic aldehyde under the conditions required for the reaction.^{42, 60, 81} o-Hydroxyphenyl ketones have been used in place of the o-hydroxybenzaldehyde in the above type of reaction.^{46, 47, 62} However, the formation of numerous by-products limits the usefulness of these ketones in the reaction.

The Knoevenagel reaction^{63, 64} between a salicylaldehyde and a malonic ester yields an ester of a 3-carboxycoumarin, equation 13. Decarboxylation of carboxycoumarins seldom proceeds smoothly and hence is not an attractive procedure for the preparation of an unsubstituted coumarin.



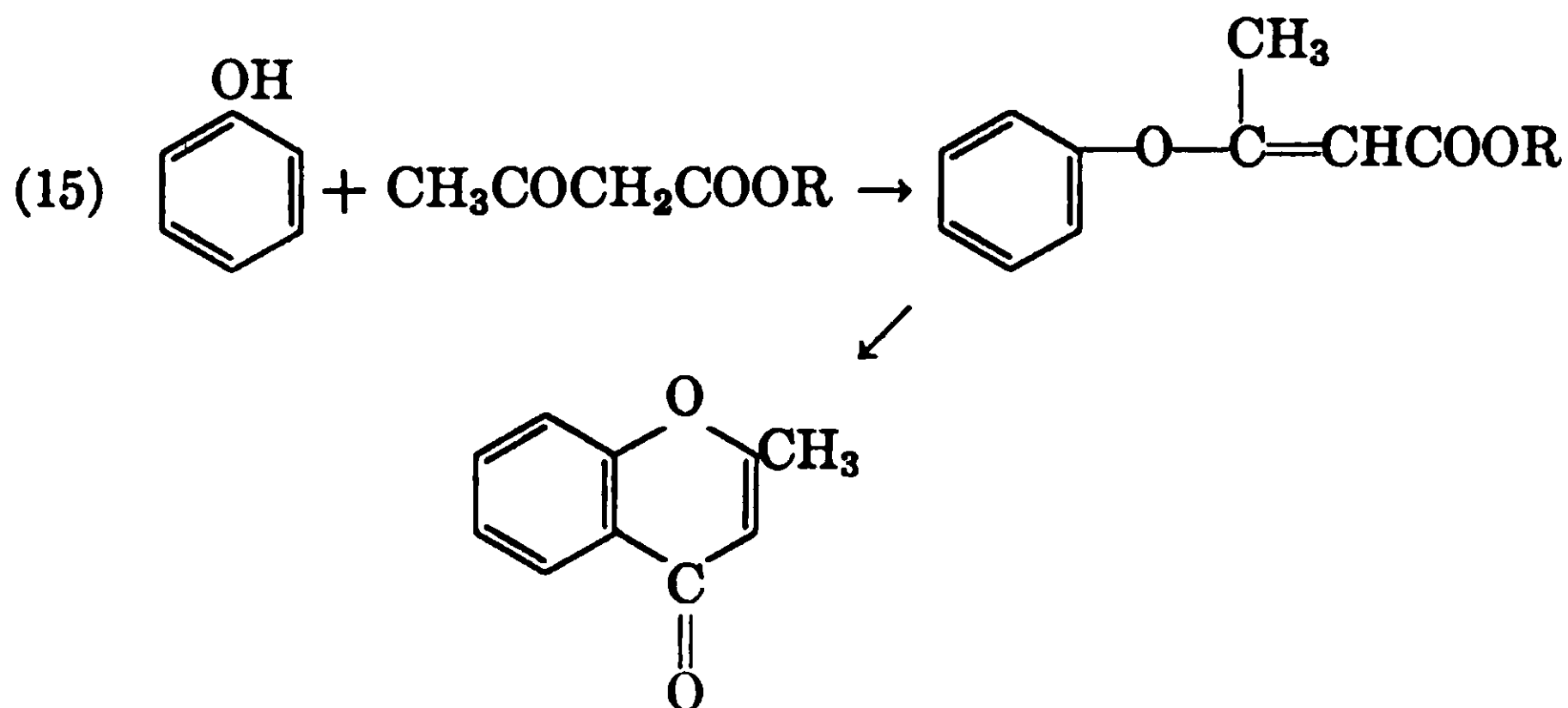
Chromones

Phosphorus pentoxide because of its powerful condensing action may cause the formation of chromones as well as coumarins by the condensation of β-keto esters with phenols, equation 14. This reaction,

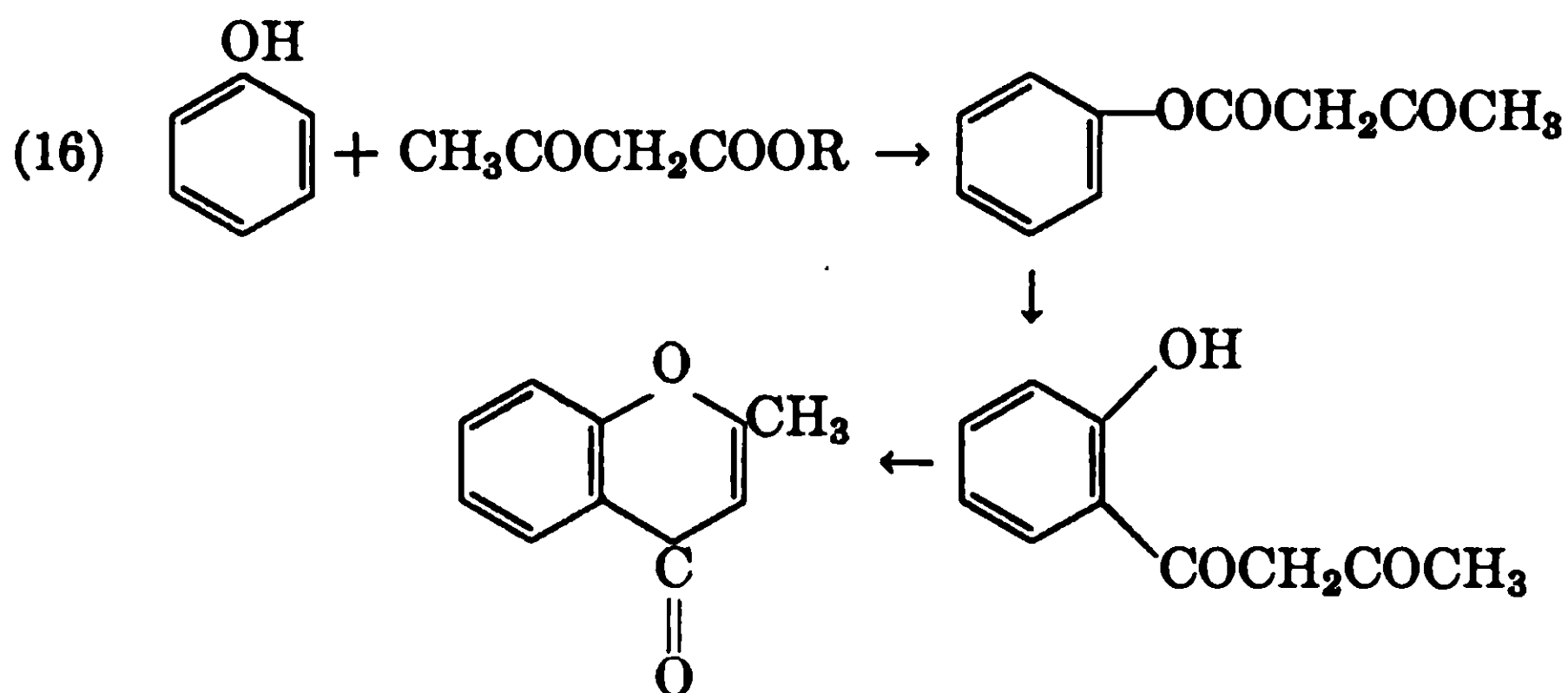


known as the Simonis reaction, has been applied to a variety of phenols.^{48-49, 61, 68-68} Frequently, phenols which give coumarins with

difficulty or which do not react with sulfuric acid as catalyst give chromones with P_2O_5 .⁶⁸ Chromone formation is also favored by the introduction of α substituents into the keto ester molecule.⁶⁹ The yields seldom exceed 30%. Robertson, Waters, and Jones⁵⁸ think that chromone formation involves the formation of a β -phenoxy-acrylic acid derivative which then gives the chromone by ring closure, equation 15. This mechanism is supported by the fact that β -phenoxy-acrylic acids may be converted to chromones.



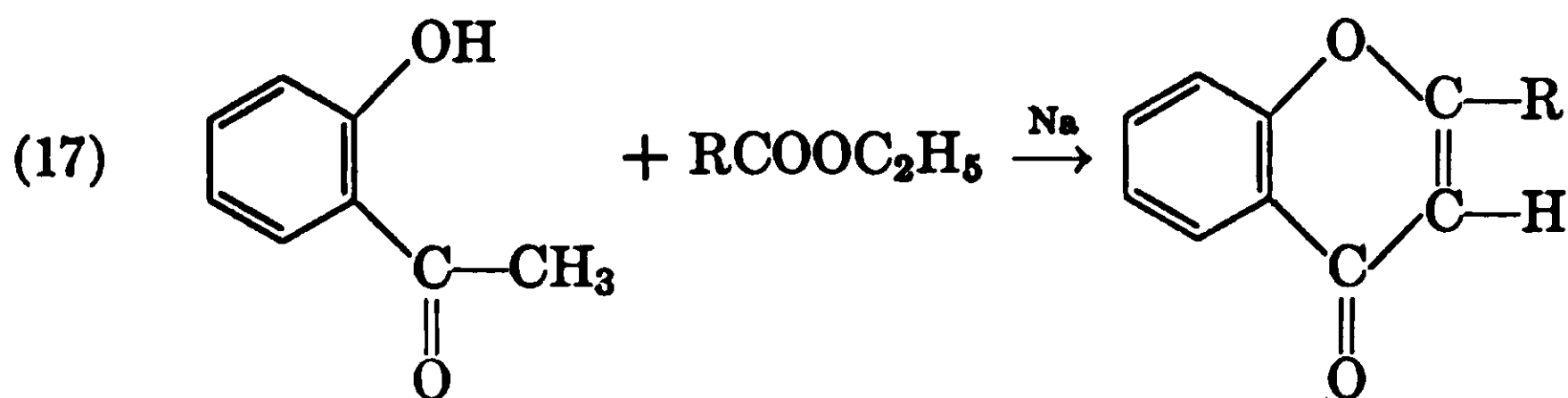
A second mechanism involves the formation of a phenyl ester, which



undergoes a Fries rearrangement to give a ketone which cyclizes,^{59, 66} reaction 16.

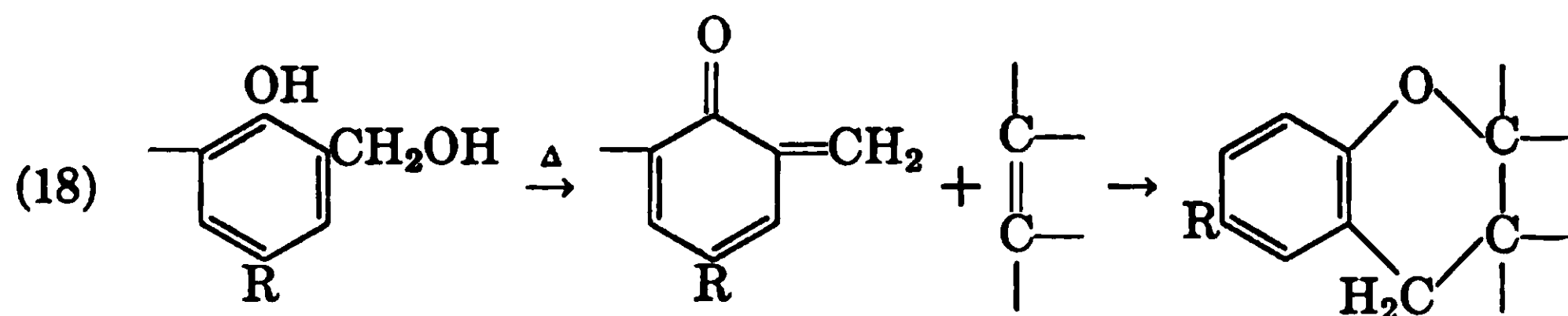
Chromones also may be obtained by reaction of *o*-hydroxyphenyl ketones with certain esters.⁷⁰⁻⁷³ Ketones such as *o*-hydroxyacetophenone, *o*-hydroxypropiophenone, *o*-hydroxybutyrophenone, and *o*-hydroxyphenylbenzyl ketone have all been used in this type of reaction, equation 17.

(Also see references 74-79.)

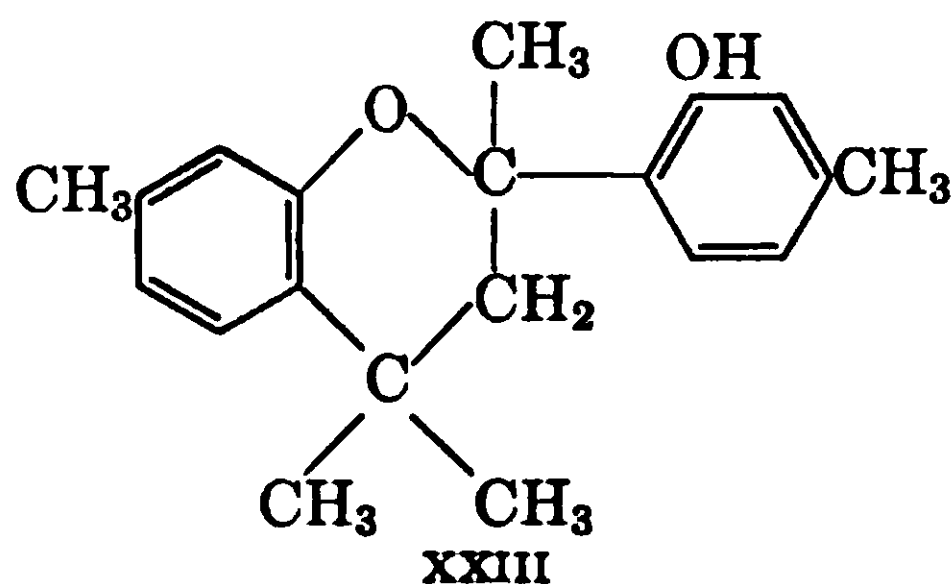


Chromans

Chroman formation is important industrially since it is involved in the reaction of drying oils with phenolic resins. Apparently an *o*-quinone methide is formed from the phenolic component. This then adds by a Diels-Alder type of reaction to a double bond of the unsaturated oil or resin, equation 18. This reaction is discussed in detail in Chapter 8.

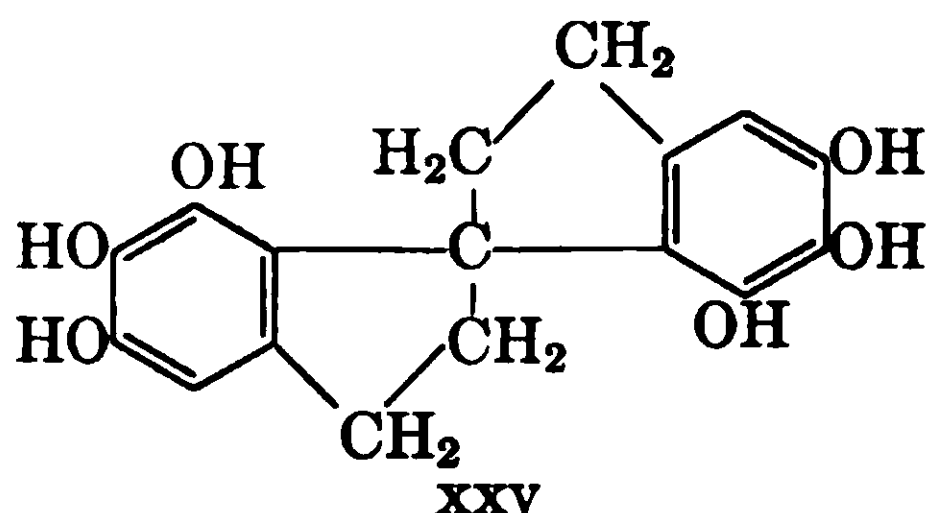
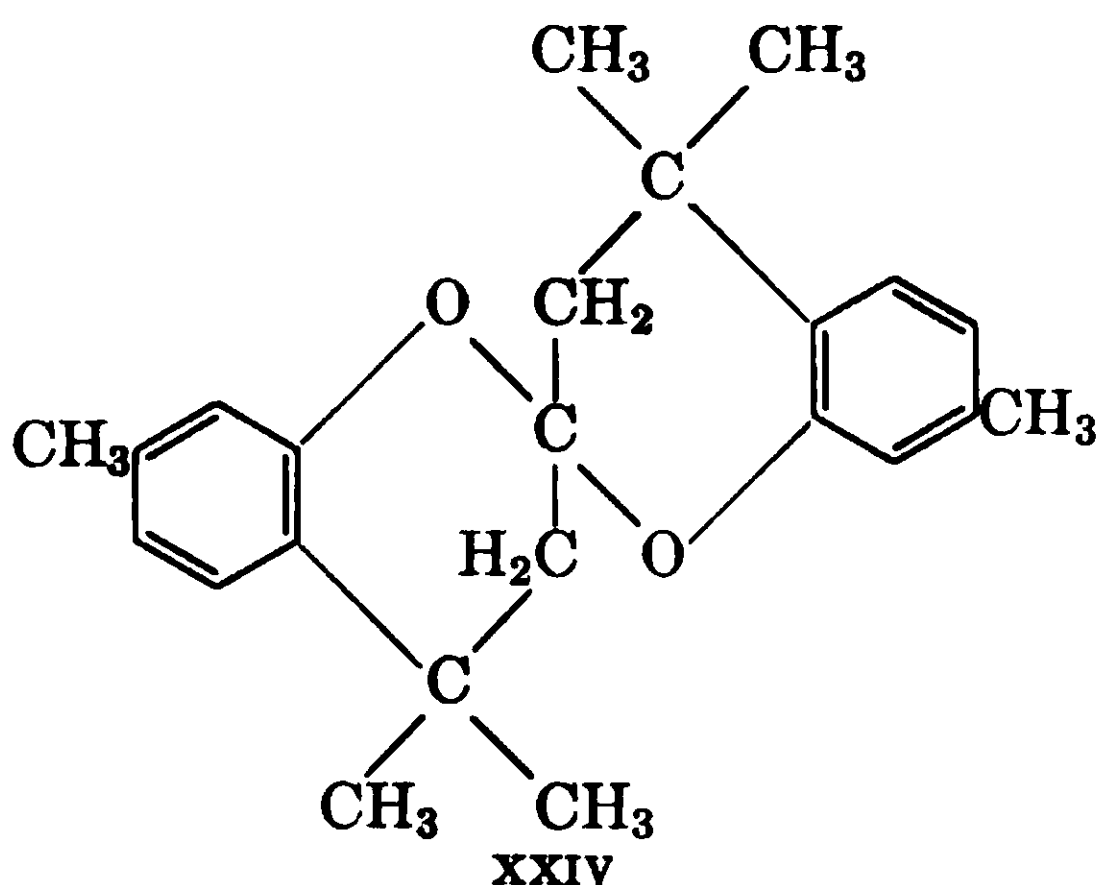


Chromans also may be obtained by the condensation of phenols with certain ketones, for example with acetone, phorone, or cyclohexanone. The condensation of phenols with acetone in particular may lead to a variety of products, depending both on the choice of reaction conditions and on the phenol. One of the most common reactions of acetone with phenols is the formation of dihydroxydiphenyl propanes. This type of reaction occurs under acidic conditions at relatively low temperatures (see Chapter 3). An excess of phenol favors this reaction. However, all phenols do not behave equally well in this reaction. For example, Baker and his coworkers found an entirely different group of materials when *m*-cresol and certain other phenols were treated with acetone.⁸⁰⁻⁸⁸ In place of a bisphenol, heterocyclic ring compounds were obtained. A substituted chroman structure, XXIII, was assigned to the product from *m*-cresol. These chro-



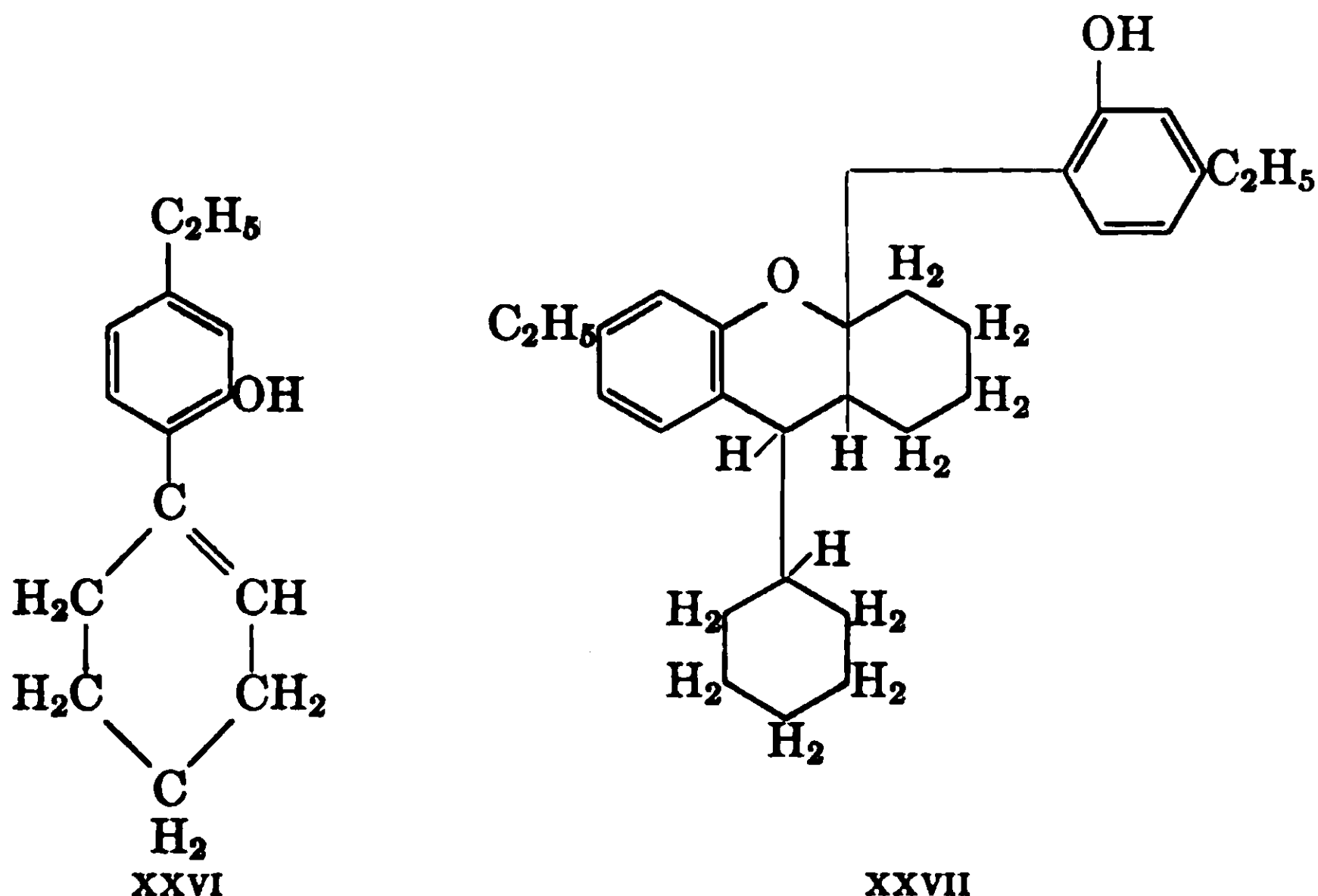
mans (flavans) form interesting one-to-one crystalline molecular complexes with many ethers, ketones, and amines.⁸²

Using aqueous hydrochloric acid as catalyst, Baker and Besly⁸⁴ obtained yet another type of product by the condensation of acetone with *m*-cresol. The product had a spirochroman structure, XXIV. *p*-Cresol and hydroxyquinol gave compounds with the same type of



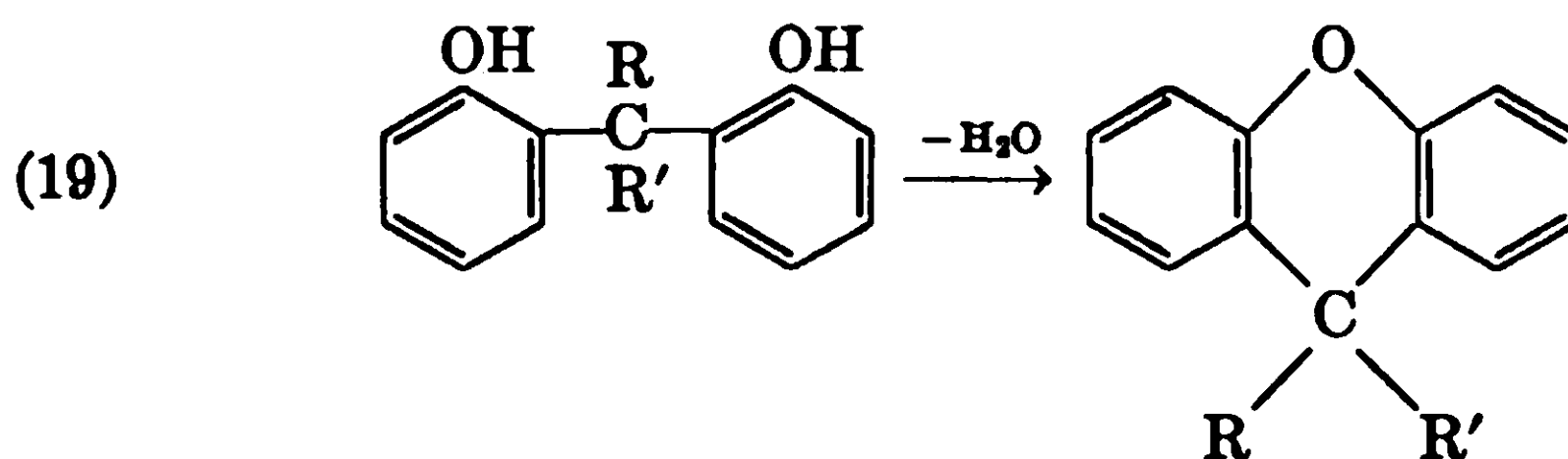
ring structure. Pyrogallol, on the other hand, reacted to form a spiroindene, XXV. Catechol and *o*-cresol behaved like pyrogallol.^{85, 86, 87} Products similar to those obtained by Baker have been reported by Fisher, Furlong, and Grant.⁸⁸ A 6-hydroxyindane was obtained when diacetone alcohol was used in place of acetone.⁸⁹ In many of the reactions discussed above, phorone may be used in place of acetone. This might be expected since acetone reacts with itself under the proper conditions to give phorone.

The condensation of cyclohexanone and *m*-ethylphenol leads to the formation of a cyclohexenylphenol, XXVI, when the reaction is conducted in acetic acid with hydrogen chloride as catalyst.^{90, 91} In the absence of a solvent the formation of a complex cyclic product with a chroman ring, XXVII, was claimed.⁹⁰



Xanthenes

Xanthenes may be prepared by several procedures, the most common being the direct reaction of phenols with aldehydes or ketones in the presence of strong acidic reagents. In each reaction the formation of a common intermediate, an *o,o'*-dihydroxydiphenylalkane, is indicated. Cyclization of an *o,o'*-dihydroxydiphenylalkane to a xanthene occurs by loss of water between the phenolic hydroxyl groups of the dihydroxydiphenylalkane, equation 19. The intermediate



bisphenol need not be isolated and frequently is difficult to separate. Basically the various procedures for preparing xanthenes differ only in the method used for obtaining the intermediate *o,o'*-dihydroxydiphenylalkane.

If the dihydroxydiphenylalkane is to be prepared as a pure compound, see Chapter 3. For the production of the xanthenes it is imperative that the phenol and reaction conditions be chosen so that an *o,o'*-dihydroxydiphenylalkane will result. For this reason the *para*-substituted phenols are most useful. Frequently a *meta* substituent,

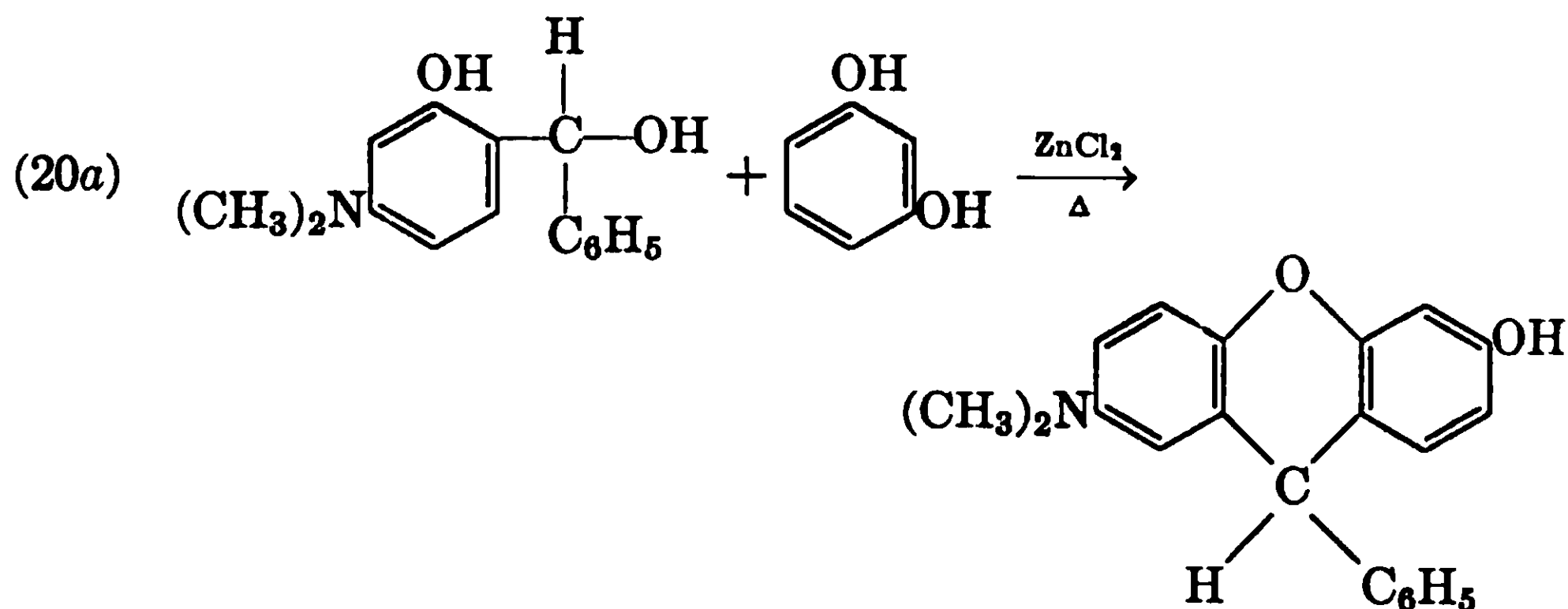
particularly if bulky, will force reaction in the *ortho* position on the opposite side of the ring. *meta*-N,N-Dimethylaminophenol is an example of such a phenol. It readily undergoes xanthene formation with various aldehydes.⁹²⁻⁹⁴

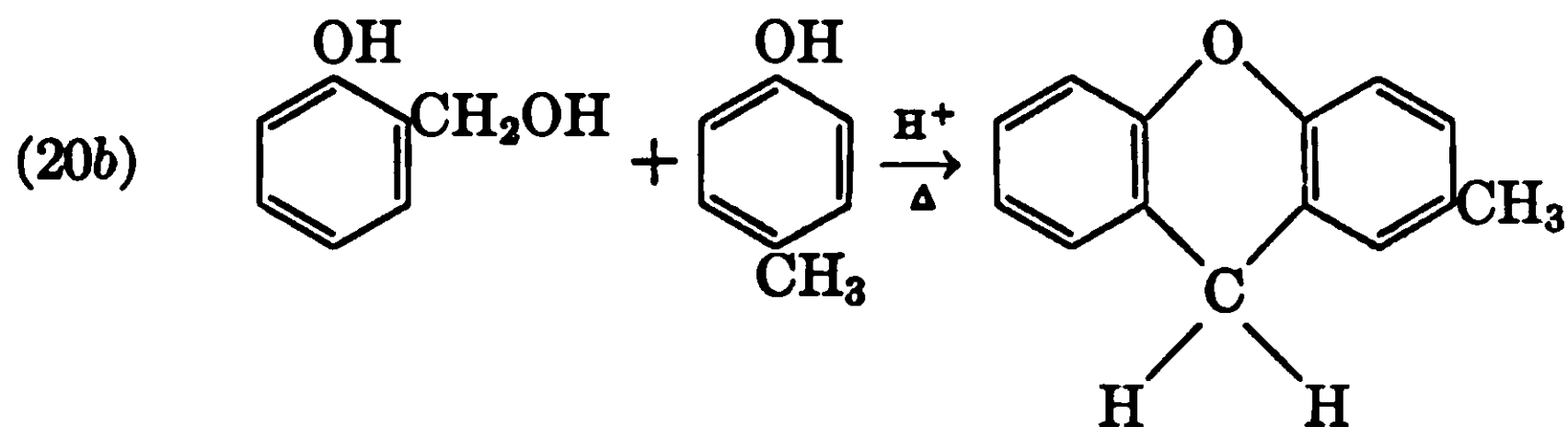
A large number of phenols have been utilized in the formation of xanthenes.⁹²⁻¹⁰⁸ The list of aldehydes and ketones that have been studied in connection with xanthene formation is also very long, including all the common lower aldehydes and ketones, benzaldehyde, salicylaldehyde, acetophenone, benzophenone, etc.^{82, 95-97, 103, 104, 106} Acetylene has been used in place of acetaldehyde on occasion.¹⁰⁹

The *o,o'*-dihydroxydiphenylalkanes may be cyclized to xanthenes by heat alone, but the reaction occurs more readily when catalysts such as zinc chloride, phosphorus oxychloride, or strong mineral acids are used.^{92, 94, 98-99, 102} Xanthene formation may occur at temperatures as low as 60–100°C., but temperatures between 150° and 200°C. are common. Without catalysts, temperatures of 250°C. or higher are required for cyclization of the dihydroxydiphenylalkanes.¹⁰⁷

Phenolic resins yield small amounts of xanthenes on pyrolysis.¹⁰⁸⁻¹⁰⁹ This indicates that the resins either contain *o,o'*-dihydroxydiphenylmethanes, as such, or that the resins are degraded to such compounds by the action of heat. It is interesting to note that Megson obtained xanthene and methylxanthene from phenolic resins long before pure 2,2'-dihydroxydiphenylmethane was obtained by the direct action of formaldehyde on phenol.¹¹⁰⁻¹¹¹ *o*-Phenol alcohols, *o,o'*-dihydroxydibenzyl ethers, and bis and tris(*o*-hydroxybenzyl)amines, all of which may be converted at least partially to *o,o'*-dihydroxydiphenylmethanes, give xanthenes on pyrolysis.

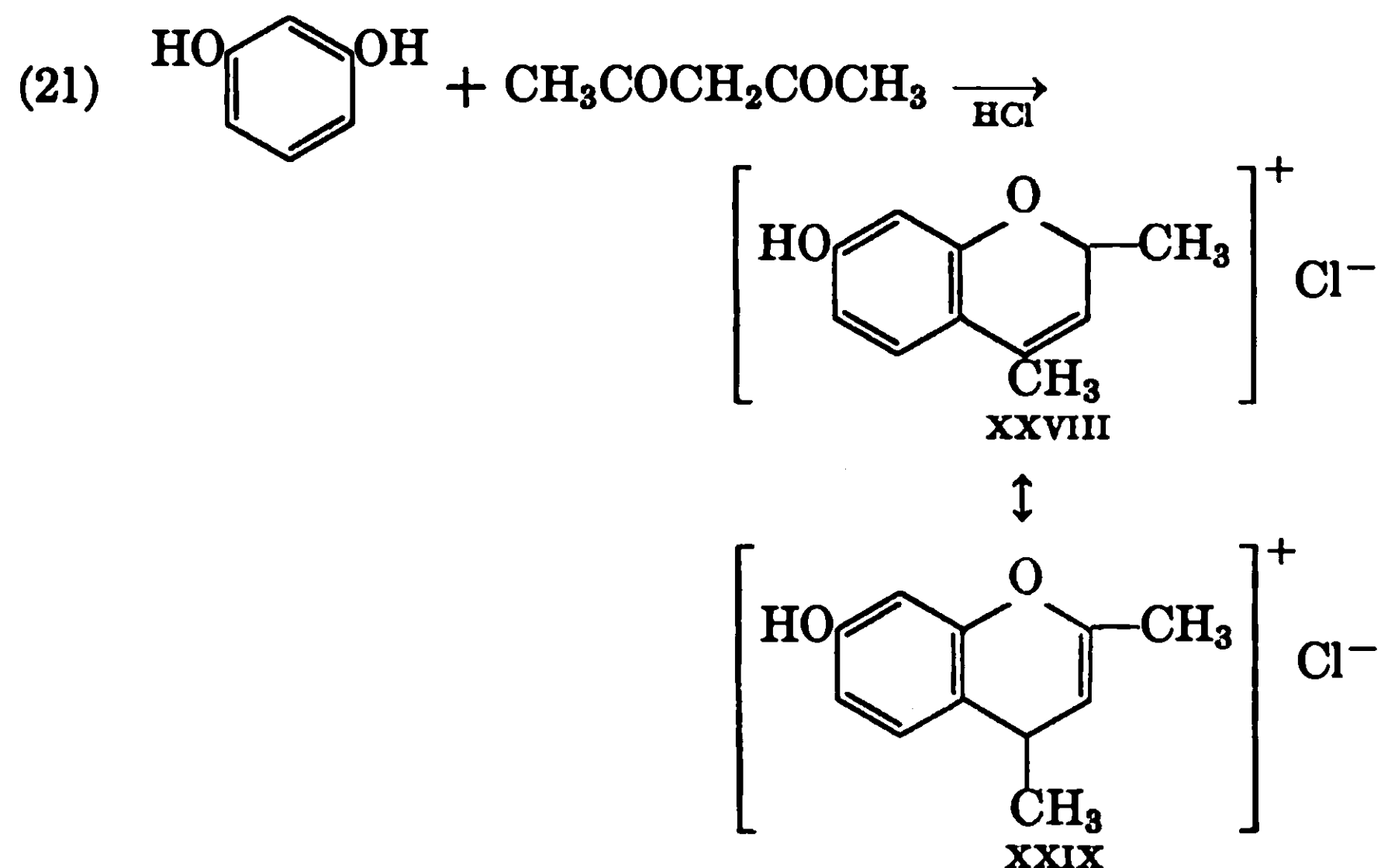
The condensation of *o*-hydroxybenzyl alcohols with phenols to give xanthenes deserves special attention. The phenol condensed with the phenol alcohol may be the same as or different from the phenol used to prepare the phenol alcohol. If the phenol is different, unsymmetrical xanthenes may be obtained,^{92, 94, 108} reactions, 20a and 20b.



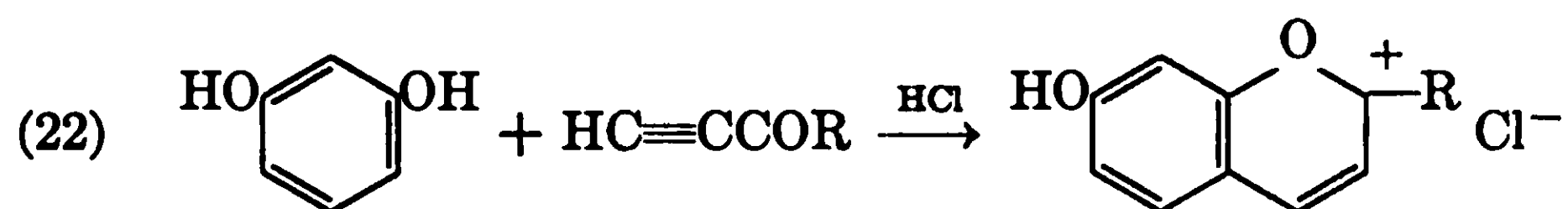


Benzopyrilium and Xanthopyrilium Salts

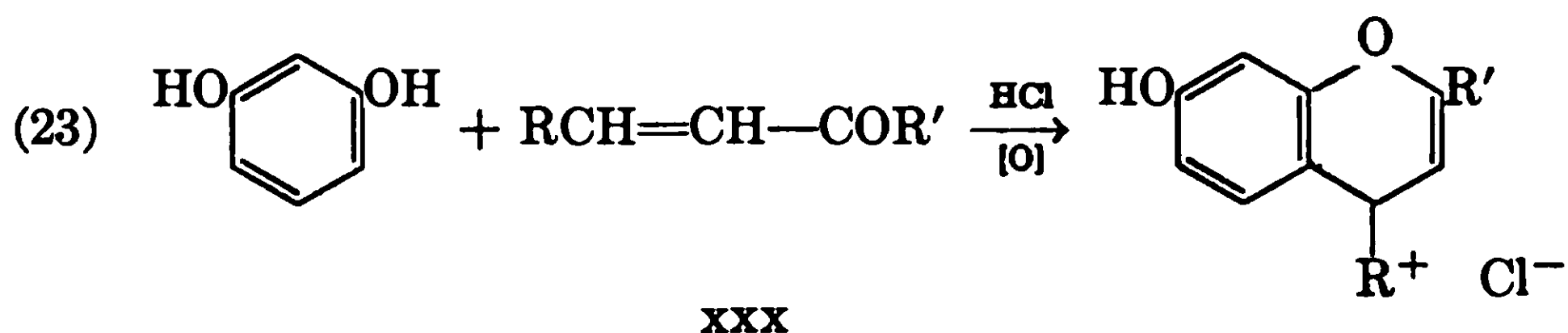
For simplicity the benzopyrilium salts will be represented as carbonium ions with formulas such as XXVIII or XXIX. The compounds may be prepared by various procedures, several of which involve the condensation of aldehydes or ketones with phenols. Because the phenols must be highly reactive the polyhydroxy phenols are usually employed.^{112, 118} Several types of ketones may be used.^{112, 114-117} The condensation of a β -dicarbonyl compound, such as acetyl acetone,^{114, 118} with resorcinol is shown in reaction 21. The reaction



requires the use of a strong acid catalyst such as dry HCl in acetic acid.¹¹⁴ Acetylenic ketones¹¹⁸ may be employed in place of the diketone, reaction 22. When an α,β -unsaturated ketone, such as XXX,

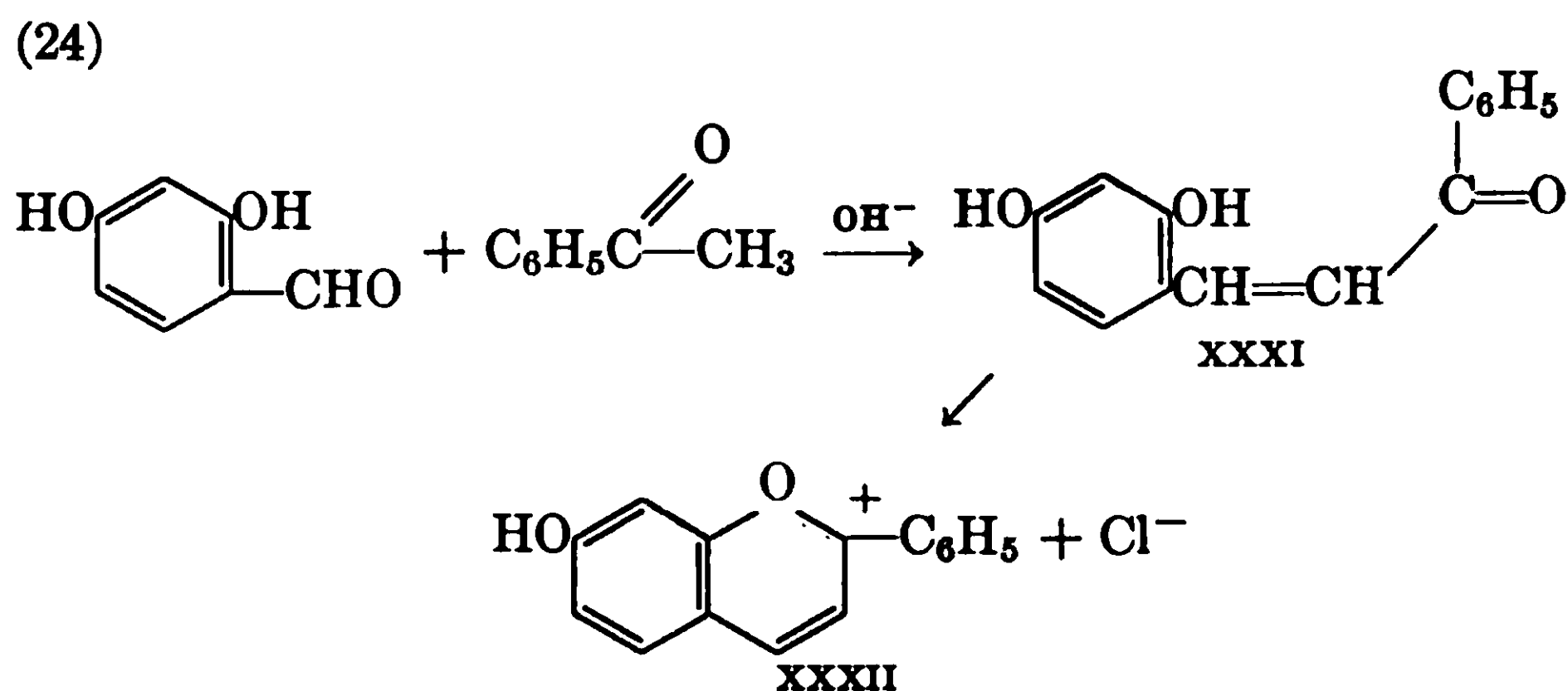


is used an oxidizing agent in addition to the acidic catalyst is required,^{119, 120} reaction 23. Chloronil is frequently used as the oxidizing

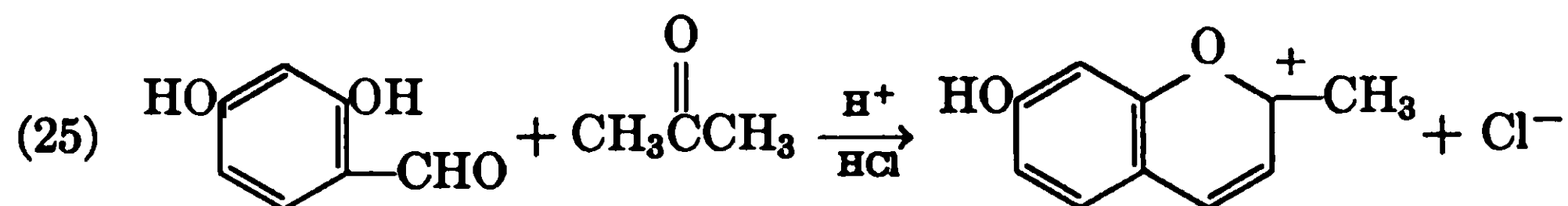


agent in such reactions, but ferric chloride, iodine, and other materials may also be employed.^{112, 112-121}

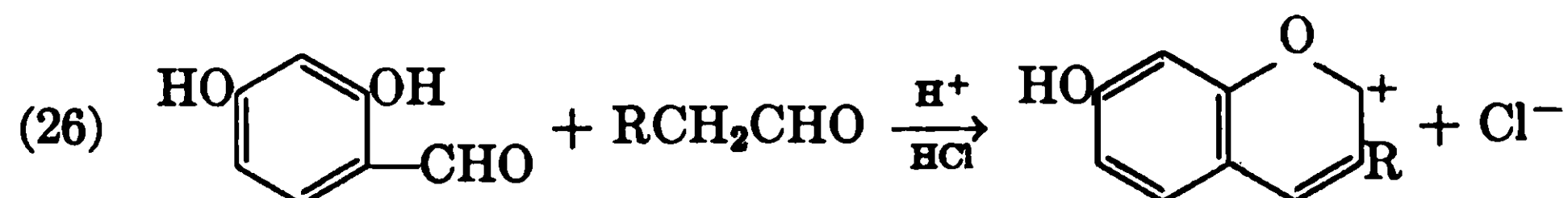
The *ortho*-hydroxybenzaldehydes, which have functional groups characteristic of both phenols and aldehydes, react with aldehydes, ketones, and α -substituted β -keto esters to give benzopyrilium salts.¹⁰² In one procedure the phenolic aldehyde was condensed with a ketone under alkaline conditions to give an unsaturated ketone, XXXI, which was then converted to the benzopyrilium salt XXXII with acid,^{122, 123} reaction 24. If acids are used for the first step of the condensation,



the benzopyrilium salt is obtained directly,¹²³ reaction 25. When

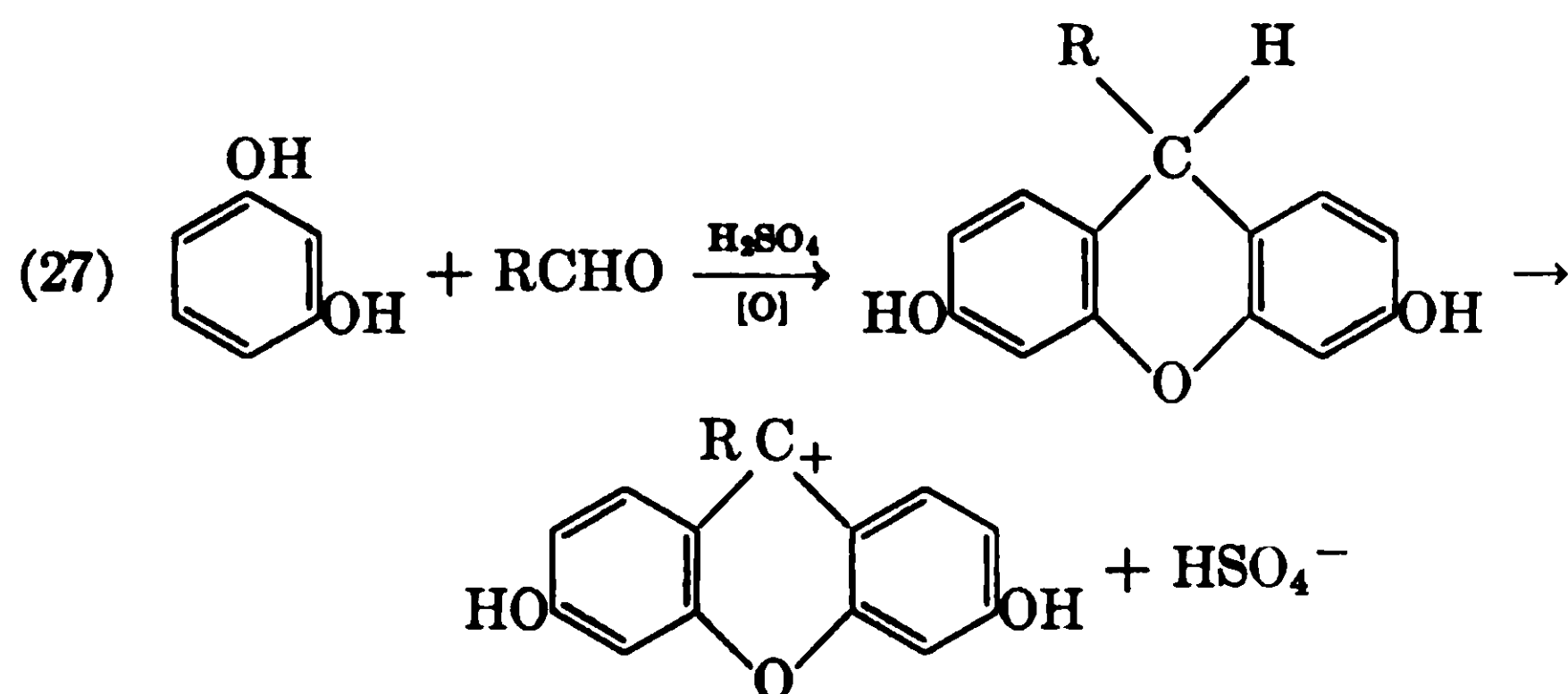


aldehydes are used in place of ketones the benzopyrilium salt has no substituent in the 2-position, reaction 26.



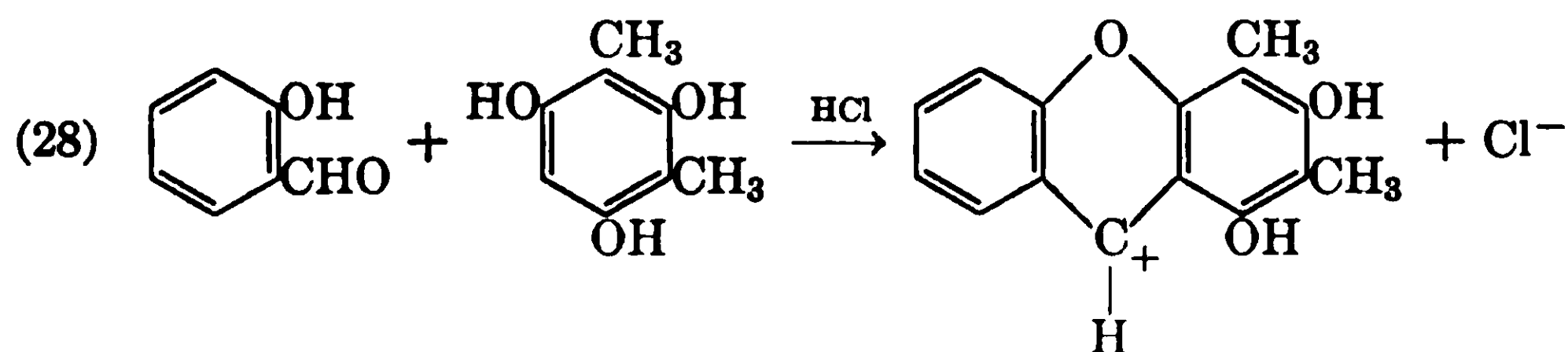
The preparation of xanthopyrilium salts is in many respects similar to the preparation of benzopyrilium salts. One of the most common

means for obtaining such compounds is by condensation of a polyhydroxyphenol with an aldehyde in the presence of an oxidizing agent, reaction 27. Sulfuric acid may serve both as the oxidizing and con-



densing agent.¹²⁴

Salicylaldehyde reacts with a highly active phenol such as dimethylphloroglucinol to give a xanthylum salt, reaction 28. In this reaction

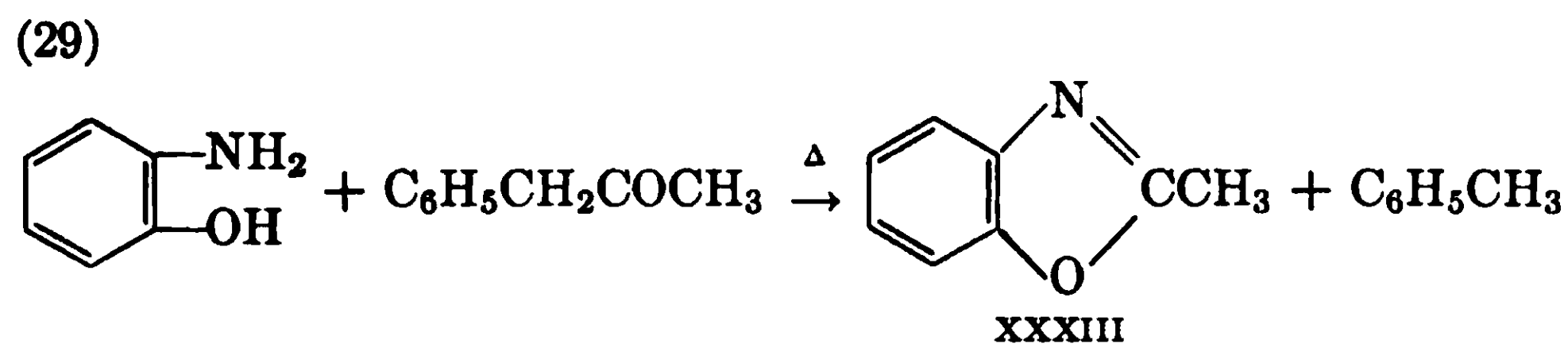


hydrochloric acid was used as catalyst.

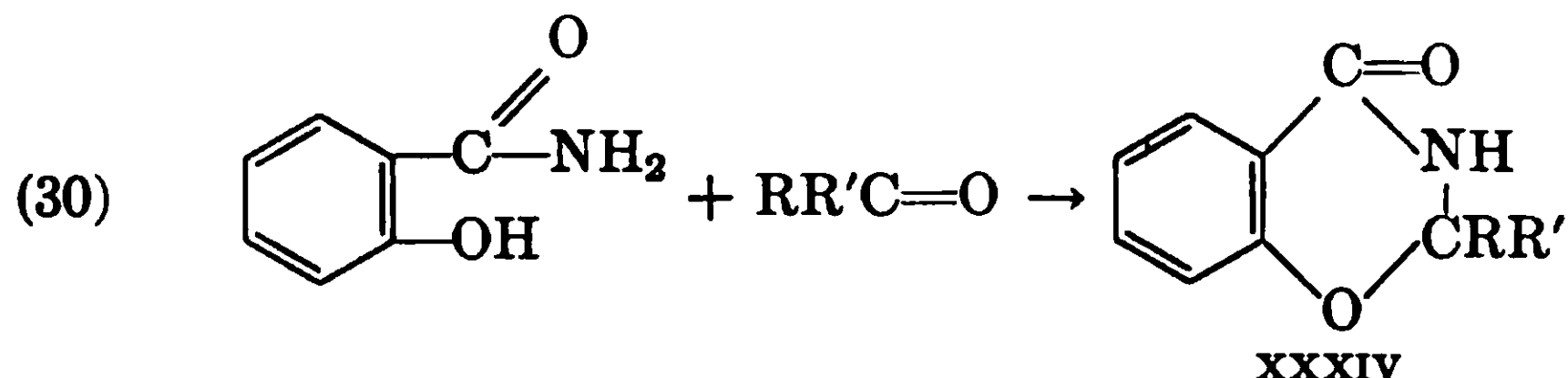
B. HETEROCYCLIC COMPOUNDS WITH NITROGEN IN RING

Compounds containing nitrogen in a heterocyclic ring joined to a benzene ring have been obtained by a condensation of phenols with aldehydes or ketones and a nitrogen-bearing compound. The nitrogen may originate either from a substituent attached to the phenol employed or may be added as a third reagent.

An example of the first type of reaction is the formation of compounds such as XXXIII.¹²⁵ When *o*-aminophenol was heated at 200–250°C. for 6 hours with benzylmethyl ketone, toluene together with the heterocyclic ring compound XXXIII was formed, reaction 29.

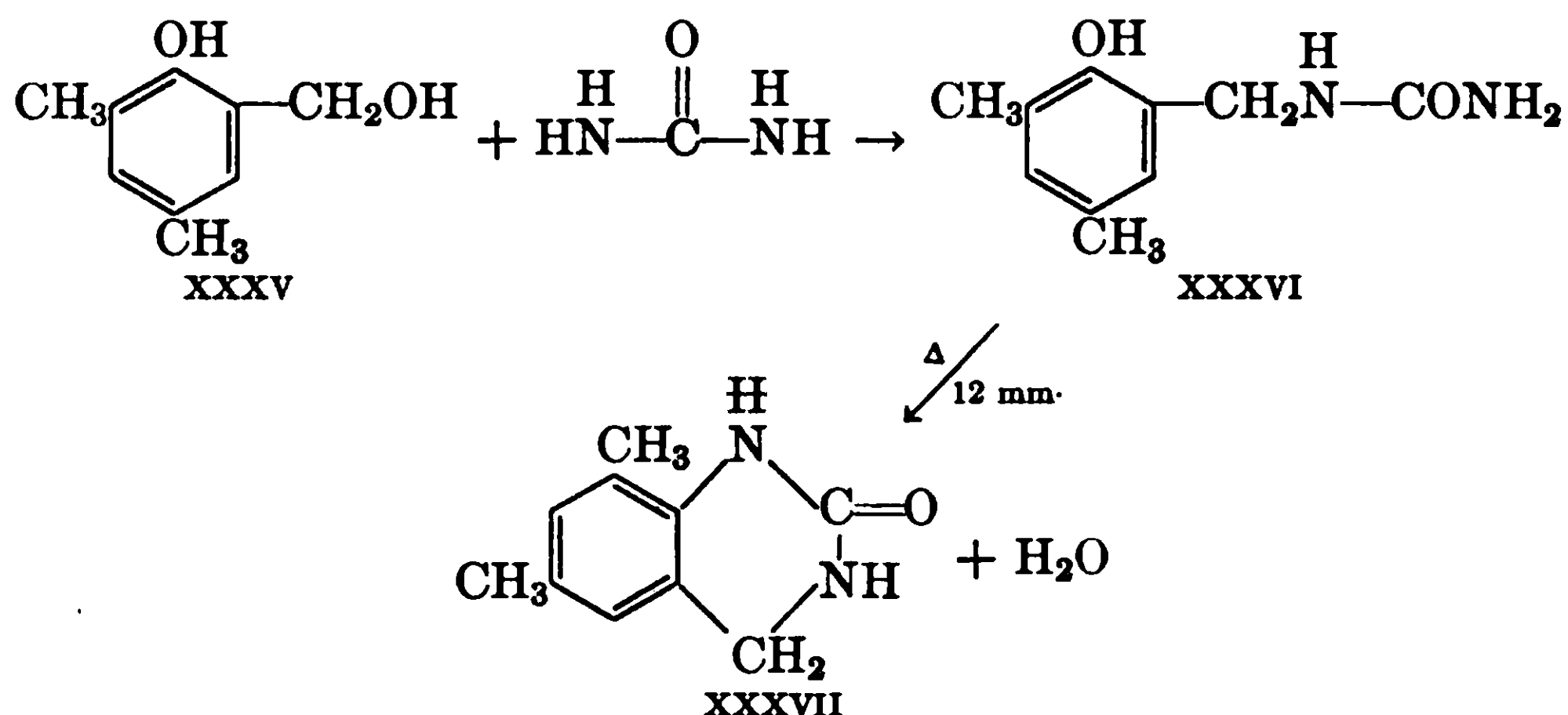


Another case in point is the reaction of salicylamide with aldehydes and ketones to give substituted 2,3-dihydro-1,3,4-benzoxaz-4-ones, XXXIV,¹²⁶⁻¹³⁰ reaction 30. The yields of dihydrobenzoxazones vary



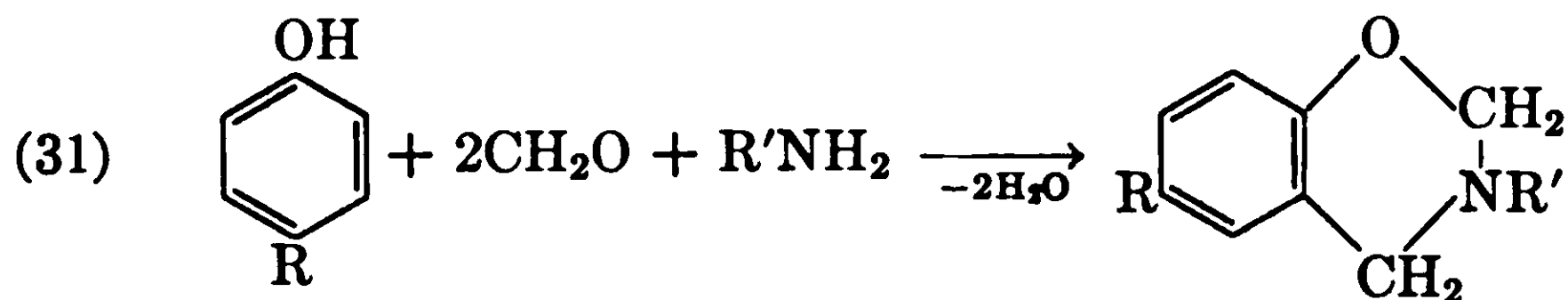
widely with the type of carbonyl compound used.¹²⁶ In general cyclic ketones and aldehydes gave better results than non-cyclic ketones. However, both types have been used.

When a third reagent is used to supply the nitrogen a phenol-aldehyde condensation product frequently can be used as a starting material. For example, Nyström¹³¹ condensed 2-hydroxy-3,5-dimethylbenzyl alcohol, XXXV, with urea and obtained the substituted urea XXXVI. That on distillation at 12 mm. gave the heterocyclic nitrogen compound XXXVII. Compounds similar to XXXVI may also

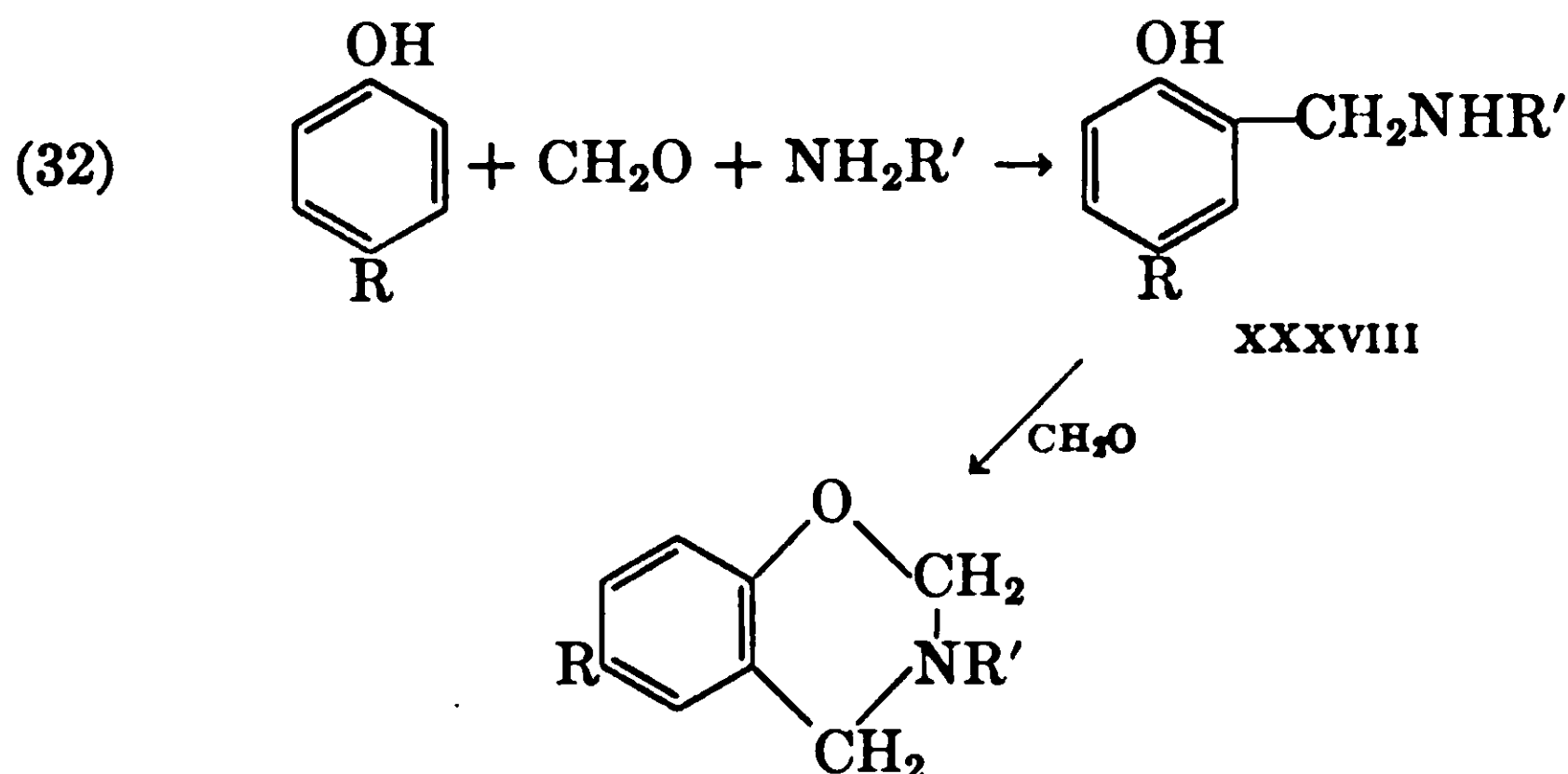


be obtained by condensation of phenols with methylolurea or urea resins.¹³²⁻¹³⁵

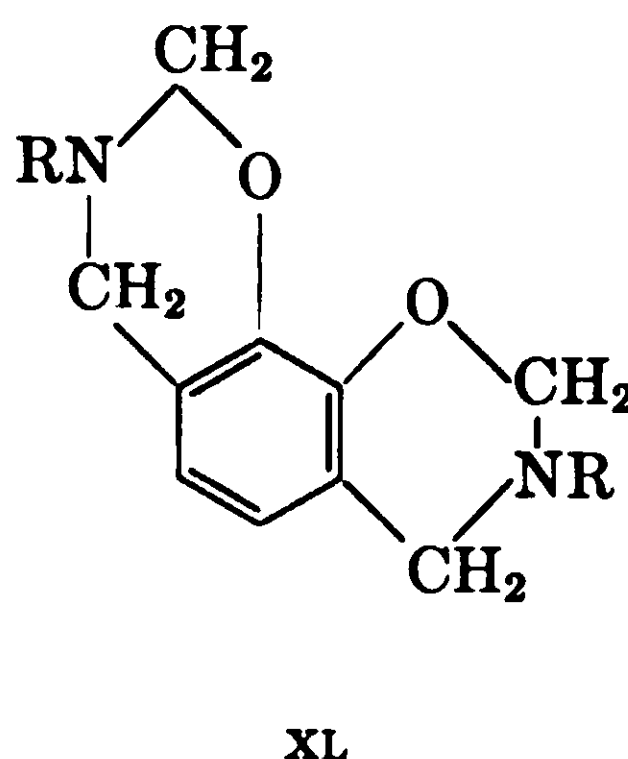
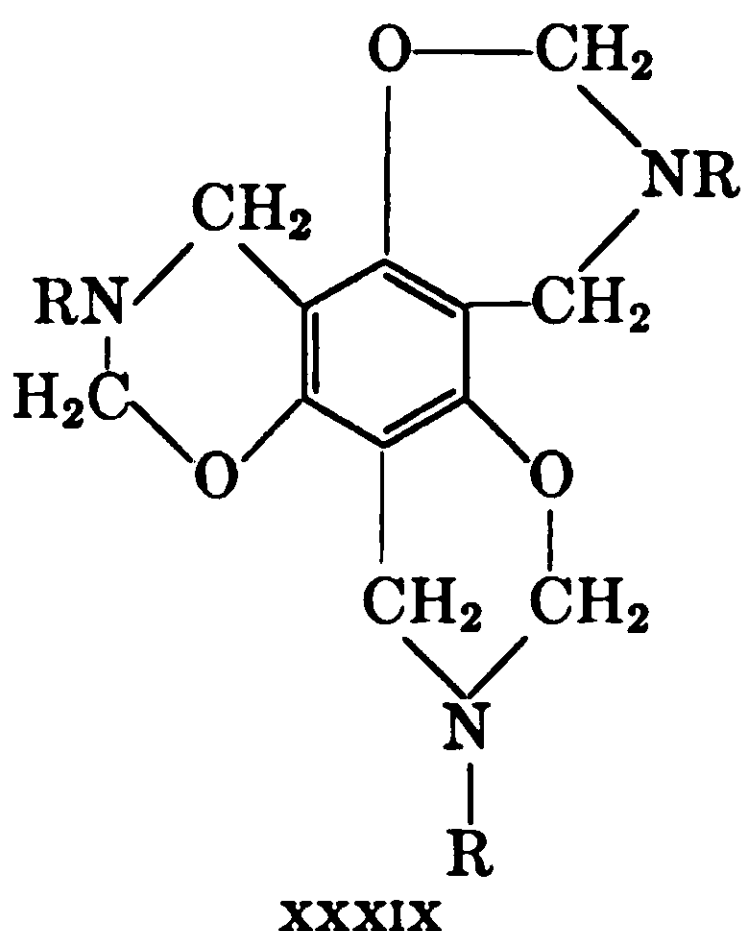
Burke and coworkers¹³⁶⁻¹⁴⁰ have studied the joint reaction of phenols with formaldehyde and primary amines (see Chapter 6). When reacted in 1:2:1 ratio, 3,4-dihydro-3,6-disubstituted 1,3-2H-benzoxazines were formed, equation 31. In an alternative procedure the



aminomethylphenol, XXXVIII, was first prepared and then reacted with formaldehyde, equation 32. This reaction is analogous to the



preparation of benzodioxans by reaction of an *ortho*-phenol alcohol with an aldehyde. When polyhydric phenols were used very complex products such as XXXIX and XL were obtained.¹⁸⁷ The four-ring compound XXXIX resulted from reaction with phloroglucinol, and the three-ring compound XL resulted from the reaction with catechol.



C. HETEROCYCLIC COMPOUNDS WITH SULFUR IN RING

Few cyclic compounds derived from phenol-aldehyde products with sulfur in the heterocyclic ring have been reported. Sultones¹⁴¹ may be formed by heating *ortho* sulfomethylated phenols, reaction 33.

- ⁸ C. A. Buehler, R. L. Brown, J. M. Holbert, J. G. Fulmer, and G. W. Parker, *J. Org. Chem.*, **6**, 902-907 (1941).
- ⁹ C. A. Buehler, F. Deebel, and R. Evans, *J. Org. Chem.*, **6**, 216-219 (1941).
- ¹⁰ C. A. Buehler, *J. Tenn. Acad. Sci.*, **22**, 303-310 (1947).
- ¹¹ E. Ziegler and K. Lercher, *Ber.*, **74**, 841-844 (1941).
- ¹² E. Ziegler and I. Simmler, *Ber.*, **74B**, 1871-1879 (1941).
- ¹³ E. Ziegler, H. Meralla, and I. Simmler, *Ber.*, **76**, 664-669 (1943).
- ¹⁴ E. Ziegler, *Ber.*, **77**, 731-735 (1944).
- ¹⁵ E. Ziegler, *Oesterr. Chem. Ztg.*, **49**, 92-102 (1948).
- ¹⁶ E. Ziegler and H. Ludde, *Monatsh.*, **79**, 55-60 (1948).
- ¹⁷ E. Ziegler and H. Ludde, *Monatsh.*, **79**, 316-322 (1948).
- ¹⁸ R. Wegler, *Angew. Chem.*, **60**, 88 (1948).
- ¹⁹ R. Wegler and K. Faber, *Ber.*, **82**, 327 (1949).
- ²⁰ W. Baker, *J. Chem. Soc.*, 1766 (1931).
- ²¹ D. R. Mehta and P. R. Ayyar, *J. Univ. Bombay*, **3**, Pt. 3, 176 (1939).
- ²² E. Adler, H. von Euler, and G. J. Gie, *Arkiv Kemi Mineral. Geol.*, **A16**, No. 12, 1-20 (1943).
- ²³ L. Haskelberg and D. Lavie, *J. Org. Chem.*, **14**, 498-503 (1949).
- ²⁴ B. Helferich and H. Liesen, *Ber.*, **83**, 567-571 (1950).
- ²⁵ V. I. Stavrovskaya and K. S. Topchiev, *Zhur. Obshchei Khim.*, **21**, 525-532 (1941).
- ²⁶ A. McGookin, A. Robertson, and T. H. Simpson, *J. Chem. Soc.*, 1951, 2021-2029.
- ²⁷ I. G. Farbenindustrie, Fr. pat. 695,602 (1930); Brit. pat. 347,887 (1931).
- ²⁸ R. Adams, M. F. Folger, and C. W. Kreger, *Chem. Zentr.*, **I**, 681 (1923).
- ²⁹ K. Hultzsich, *Kunststoffe*, **39**, 57-63 (1949).
- ³⁰ M. P. Balfe and W. C. Weber, *J. Chem. Soc.*, 1942, 718.
- ³¹ G. Sloof, *Rec. trav. chim.*, **54**, 995 (1935); J. Böeeken and G. Sloof, *Proc. Acad. Sci. Amsterdam*, **37**, 584-590 (1934).
- ³² M. Kohn, *J. Am. Chem. Soc.*, **73**, 480-481 (1951).
- ³³ V. B. Meyer in Elderfield, *Heterocyclic Compounds*, Vol. 2, John Wiley & Sons, New York, 1951, pp. 7-65.
- ³⁴ F. R. Japp and A. N. Meldrum, *J. Chem. Soc.*, **75**, 1035-1043 (1899).
- ³⁵ E. Adler and S. Tingstam, *Arkiv Kemi Mineral. Geol.*, **B16**, No. 18, 1-7 (1943).
- ³⁶ D. W. Clayton, W. E. Elston, R. Ghosh, and B. C. Platt, *J. Chem. Soc.*, 1953, 581-586.
- ³⁷ J. B. Niederl and V. Niederl, *J. Am. Chem. Soc.*, **61**, 348-350 (1939).
- ³⁸ K. Sisido, H. Nozaki, and I. Iwako, *J. Am. Chem. Soc.*, **71**, 2037-2041 (1949).
- ³⁹ D. R. Stevens and A. C. Dubbs, U. S. pat. 2,515,909 (1950).
- ⁴⁰ J. T. Hewitt and F. G. Pope, *J. Chem. Soc.*, **69**, 1265-1269 (1896); **71**, 1086 (1897).
- ⁴¹ H. von Pechmann and C. Duisberg, *Ber.*, **16**, 2119-2128 (1883).
- ⁴² S. Wawzonek in Elderfield, *Heterocyclic Compounds*, Vol. 2, John Wiley & Sons, New York, 1951, pp. 181-186.
- ⁴³ S. Sethna and R. Phadke in Adams, *Organic Reactions*, Vol. 7, John Wiley & Sons, New York, 1953, pp. 1-58.
- ⁴⁴ C. R. Jacobson, K. R. Brown, and E. D. Amstutz, *J. Org. Chem.*, **18**, 1117 (1953).
- ⁴⁵ A. Robertson, R. B. Waters, and E. T. Jones, *J. Chem. Soc.*, 1932, 1681-1688.

- ⁴⁶ S. Sethna and N. M. Shah, *J. Indian Chem. Soc.*, **17**, 487 (1940).
⁴⁷ Heilbrow, Hey, and Lythgoe, *J. Chem. Soc.*, 1936, 295.
⁴⁸ S. M. Sethna, N. M. Shah, and R. C. Shah, *J. Chem. Soc.*, 1938, 228-232.
⁴⁹ Desai and Ekhlās, *Proc. Indian Acad. Sci.*, **8A**, 567 (1938).
⁵⁰ H. von Pechmann and E. Graeger, *Ber.*, **34**, 378-386 (1901).
⁵¹ K. Fries and W. Klostermann, *Ber.*, **39**, 871-875 (1906).
⁵² D. W. Clayton, *J. Chem. Soc.*, 1908, 2016.
⁵³ C. F. Koelsch and C. R. Stevens, *J. Am. Chem. Soc.*, **72**, 2209-2212 (1950).
⁵⁴ C. Mentzer, D. Molho, and P. Vercier, *Bull. soc. chim. France*, 1949, 749-754.
⁵⁵ C. Mentzer and P. Vercier, *Compt. rend.*, **232**, 1674-1676 (1951).
⁵⁶ P. Vercier, D. Molho, and C. Mentzer, *Bull. soc. chim. France* 1950, 1248-1253.
⁵⁷ V. M. Dixit, A. M. Kanduti, and L. M. Mulay, *J. Indian Chem. Soc.*, **22**, 207 (1945).
⁵⁸ A. Robertson, R. B. Waters, and E. T. Jones, *J. Chem. Soc.*, 1932, 1681-1688.
⁵⁹ S. Z. Ahmed and R. D. Desai, *Proc. Indian Acad. Sci.*, **6A**, 6 (1937).
⁶⁰ E. Späth, *Ber.*, **70A**, 83 (1937).
⁶¹ J. R. Johnson in Adams, *Organic Reactions*, Vol. 1, John Wiley & Sons, New York, 1942, p. 210.
⁶² F. W. Canter, A. R. Martin, and A. Robertson, *J. Chem. Soc.*, 1931, 1877.
⁶³ T. Boehm and E. Profft, *Arch. Pharm.*, **269**, 25 (1931).
⁶⁴ E. Knoevenagel, *Ber.*, **37**, 4461 (1904).
⁶⁵ E. Petschek and H. Simonis, *Ber.*, **46**, 2014 (1913).
⁶⁶ S. Wawzonek in Elderfield, *Heterocyclic Compounds*, Vol. 2, John Wiley & Sons, New York, 1951, pp. 185, 251-252.
⁶⁷ J. Schmutz, H. Lauener, R. Hirt, and M. Sanz, *Helv. Chim. Acta*, **34**, 767-779 (1951).
⁶⁸ D. Chakravarti, *J. Indian Chem. Soc.*, **9**, 25, 31, 390 (1932).
⁶⁹ D. Chakravarti and B. Banerjee, *J. Indian Chem. Soc.*, **13**, 619 (1936).
⁷⁰ E. Späth and E. Lederer, *Ber.*, **63**, 743 (1930).
⁷¹ V. S. Cheema and K. Venkataraman, *J. Chem. Soc.*, 1932, 918.
⁷² H. S. Mahal, H. S. Rai, and K. Venkataraman, *J. Chem. Soc.*, 1934, 1120, 1769.
⁷³ C. Mentzer and P. Meunier, *Bull. soc. chim. France*, (5), **11**, 302 (1944).
⁷⁴ S. Fujise, M. Suzulsi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 1073-1075 (1951).
⁷⁵ E. Bonifazi, St. v. Kostanecki, and J. Tambor, *Ber.*, **39**, 86 (1906).
⁷⁶ G. Zemplén, L. Mester, and E. Kardos, *Ber.*, **77**, 457 (1944).
⁷⁷ I. Z. Saiyad, D. R. Nadkarni, and T. S. Wheeler, *J. Chem. Soc.*, 1937, 1737.
⁷⁸ Y. Kimura, *J. Pharm. Soc. Japan*, **58**, 123 (1938).
⁷⁹ L. Reichel, et al., *Ber.*, **74**, 1741, 1802 (1941); **76**, 1134 (1943).
⁸⁰ W. Baker and D. W. Besly, *J. Chem. Soc.*, 1940, 1103-1106.
⁸¹ W. Baker, R. F. Curtis, and J. F. W. McOmie, *J. Chem. Soc.*, 1951, 76-83.
⁸² W. Baker, R. F. Curtis, and M. C. Edwards, *J. Chem. Soc.*, 1951, 83-87.
⁸³ W. Baker, D. F. Downing, A. E. Hewitt-Symonds, and J. F. W. McOmie, *J. Chem. Soc.*, 1952, 3796.
⁸⁴ W. Baker and D. M. Besly, *J. Chem. Soc.*, 1939, 195-199.
⁸⁵ W. Baker, *J. Chem. Soc.*, 1934, 1678-1681.
⁸⁶ W. Baker and J. C. McGowan, *J. Chem. Soc.*, 1938, 347-353.
⁸⁷ W. Baker and D. M. Besly, *J. Chem. Soc.*, 1939, 1421-1424.

- ⁸⁸ C. H. Fisher, R. W. Furlong, and M. Grant, *J. Am. Chem. Soc.*, **58**, 820 (1036).
- ⁸⁹ J. B. Niederl, V. Niederl, and S. Reznick, *J. Am. Chem. Soc.*, **58**, 667-659 (1036).
- ⁹⁰ J. B. Niederl and A. Ziering, *J. Am. Chem. Soc.*, **62**, 1157-1158 (1040).
- ⁹¹ J. B. Niederl and V. Niederl, *J. Am. Chem. Soc.*, **61**, 1785-1788 (1030).
- ⁹² T. B. Downey and A. Lowy, *J. Am. Chem. Soc.*, **45**, 1060 (1023).
- ⁹³ J. Biehringer, *J. prakt. Chem.*, (2), **54**, 217 (1806).
- ⁹⁴ S. Krishna and F. G. Pope, *J. Chem. Soc.*, **119**, 286 (1021).
- ⁹⁵ W. Feuerstein and A. Lipp, *Ber.*, **35**, 3252 (1002).
- ⁹⁶ R. N. Sen, N. C. Chattopadhyaya, and H. K. Sen-Gupta, *J. Indian Chem. Soc.*, **7**, 007 (1030).
- ⁹⁷ R. N. Sen and N. N. Sinha, *J. Am. Chem. Soc.*, **45**, 2084-2906 (1023).
- ⁹⁸ W. Wolff, *Ber.*, **26**, 83 (1803).
- ⁹⁹ G. W. Clough, *J. Chem. Soc.*, **89**, 771 (1006).
- ¹⁰⁰ E. Claisen, *Ann.*, **237**, 261 (1887).
- ¹⁰¹ L. Kahl, *Ber.*, **1898**, 143.
- ¹⁰² C. A. Buehler, D. E. Cooper, and E. O. Scrudder, *J. Org. Chem.*, **8**, 316 (1943).
- ¹⁰³ H. K. Sen-Gupta, *J. Chem. Soc.*, **105**, 399 (1914).
- ¹⁰⁴ R. Meyer and K. Witte, *Ber.*, **41**, 2453 (1908).
- ¹⁰⁵ R. N. Sen and N. N. Sakar, *J. Am. Chem. Soc.*, **47**, 1079-1091 (1925).
- ¹⁰⁶ S. A. Flood and J. A. Nieuwland, *J. Am. Chem. Soc.*, **50**, 2566 (1928).
- ¹⁰⁷ K. Hultsch, *Chemie der Phenolhärze*, Springer-Verlag, 1950.
- ¹⁰⁸ N. J. L. Megson, *Trans. Faraday Soc.*, **32**, 336-345 (1936).
- ¹⁰⁹ N. J. L. Megson, *J. Soc. Chem. Ind.*, **58**, 131-139 (1939).
- ¹¹⁰ H. L. Bender and A. G. Farnham, U. S. pat. 2,475,587 (1949).
- ¹¹¹ H. L. Bender, *Modern Plastics*, February, 1953, 136-138, 220-222; March, 1954, 115-118, 200.
- ¹¹² H. Decker and P. Becker, *Ber.*, **47**, 2288 (1914).
- ¹¹³ S. Wawzonek in Elderfield, *Heterocyclic Compounds*, Vol. 2, John Wiley & Sons, New York, 1951, pp. 279-282, 468-477.
- ¹¹⁴ J. S. Buck and I. M. Heilbron, *J. Chem. Soc.*, **123**, 2521 (1923).
- ¹¹⁵ C. Bulow and H. Wagner, *Ber.*, **34**, 1189 (1901).
- ¹¹⁶ M. Healey and R. Robinson, *J. Chem. Soc.*, **1934**, 1625.
- ¹¹⁷ C. Bulow and W. von Sicherer, *Ber.*, **34**, 2368, 3916 (1901).
- ¹¹⁸ A. W. Johnson and R. M. Melhuish, *J. Chem. Soc.*, **1947**, 346.
- ¹¹⁹ A. Lowenbein, *Ber.*, **1924**, 1517.
- ¹²⁰ R. Robinson and J. Walker, *J. Chem. Soc.*, **1934**, 1435-1440.
- ¹²¹ H. Appel and R. Robinson, *J. Chem. Soc.*, **1935**, 426.
- ¹²² H. Decker and Th. von Fellenberg, *Ann.*, **1907**, 356, 281.
- ¹²³ H. Decker and Th. von Fellenberg, *Ber.*, **40**, 3815 (1907).
- ¹²⁴ M. Fieser and L. F. Fieser, *J. Am. Chem. Soc.*, **63**, 1572 (1941).
- ¹²⁵ K. J. Kreysa, V. F. Maturi, J. J. Finn, J. J. McClaron, and F. Lombard, *J. Am. Chem. Soc.*, **73**, 1155 (1951).
- ¹²⁶ B. W. Horrom and H. E. Zaugg, *J. Am. Chem. Soc.*, **72**, 721 (1950).
- ¹²⁷ A. W. Titherley, *J. Chem. Soc.*, **1907**, 1419-1433.
- ¹²⁸ C. A. Keane and W. W. S. Nichols, *J. Chem. Soc.*, **1907**, 264-271.
- ¹²⁹ W. L. Hicks, *J. Chem. Soc.*, **1910**, 1032-1034.
- ¹³⁰ H. O. L. Fischer, G. Daugschat, and H. Stettiner, *Ber.*, **65**, 1032-1037 (1932).
- ¹³¹ H. Nyström, *Kunststoff-Tech. u. Kunststoff-Anwend.*, **12**, 81-84 (1942).

- ¹³² H. von Diesbach, Ger. pat. 511,210 (1928).
- ¹³³ B. A. Arbuzov and D. A. Livshits, *Izvest. Akad. Nauk S.S.S.R.*, 1946, 391-402.
- ¹³⁴ G. Zigeuner, *Monatsh.*, 82, 175-176 (1951).
- ¹³⁵ G. Zigeuner, *Kunststoffe*, 41, 221-224 (1951).
- ¹³⁶ W. J. Burke, *J. Am. Chem. Soc.*, 71, 609 (1949).
- ¹³⁷ W. J. Burke and C. Weatherbee, *J. Am. Chem. Soc.*, 72, 4691-4694 (1950).
- ¹³⁸ W. J. Burke, M. J. Kolbezen, and C. W. Stephens, *J. Am. Chem. Soc.*, 74, 3601 (1952).
- ¹³⁹ W. J. Burke, R. P. Smith, and C. Weatherbee, *J. Am. Chem. Soc.*, 74, 601 (1952).
- ¹⁴⁰ W. J. Burke and C. W. Stephens, *J. Am. Chem. Soc.*, 74, 1518 (1952).
- ¹⁴¹ E. A. Shearing and S. Smiles, *J. Chem. Soc.*, 1937, 1348-1357.
- ¹⁴² V. Ettel and J. Weichet, *Collection Czechoslov. Chem. Commun.*, 13, 433-441 (1948).

C H A P T E R E I G H T

The Reaction of Phenolic Resins with Unsaturated Compounds

The most important products derived from phenolic resins and unsaturated compounds are those used in surface coatings where the unsaturated compound is a drying oil.¹⁻⁵ As we know them today, these combinations possess many of the more desirable properties of both materials. The phenolic resins impart body, strength, toughness, solvent and moisture resistance, and durability; the oil imparts flexibility and air-drying and film-forming properties. The development of such combinations stems from an early desire to use phenolic resins as substitutes for shellac. This was never fully achieved because of the inherent brittleness of the phenolic resins and lack of certain other desirable properties possessed by shellac. In an effort to improve the flexibility of the phenolic resins, plasticization with oils was tried. The early experiments along these lines were disappointing in that the oils were not compatible with the phenolic resins then in use.

Berend⁶ made the important observation around 1910 that fusion of a phenolic resin with rosin imparted oil solubility to the fusion product. The first resins used were the conventional solid resins then available. The fusion products were dark in color and not very uniform. It was soon found best to make liquid resoles and react directly with rosin to form hard, light-colored varnish resins. The melting point of the fusion product was increased appreciably by esterification with a polyol such as glycerine. These resins were first produced by the firm of Kurt Albert in Germany. There they were referred to as Albertols or Albertol acids, depending on whether or not the resins were esterified.⁷ The commercial Albertols and Amberols are of this type and are still in use for the preparation of 4-hour varnishes and enamels. These modified phenolic resins were introduced in America by the Resinous Products Co. in 1924.

In 1928 the Bakelite Corp. introduced a new type of oil-soluble resin, based on products from the condensation of formaldehyde, preferably under mildly acidic conditions, with an alkyl- or aryl-

substituted phenol. The alkyl or aryl substituent imparted sufficient oil solubility to the resin so that homogeneous varnishes could be prepared, frequently with only mild cooking. The *para*-substituted phenols were preferred over their *ortho* isomers since the derived resins were less susceptible to yellowing during the cooking operation and subsequent weathering of the films. One of the most important early resins of this type, described in a U. S. patent⁸ issued to Turkington and Butler in 1935, was derived from *p*-phenylphenol. This resin still holds a prominent place among oil-soluble resins. Since the resins based on substituted phenols did not require fusion with rosin or other resins to develop oil solubility they were referred to as "100% phenolic."

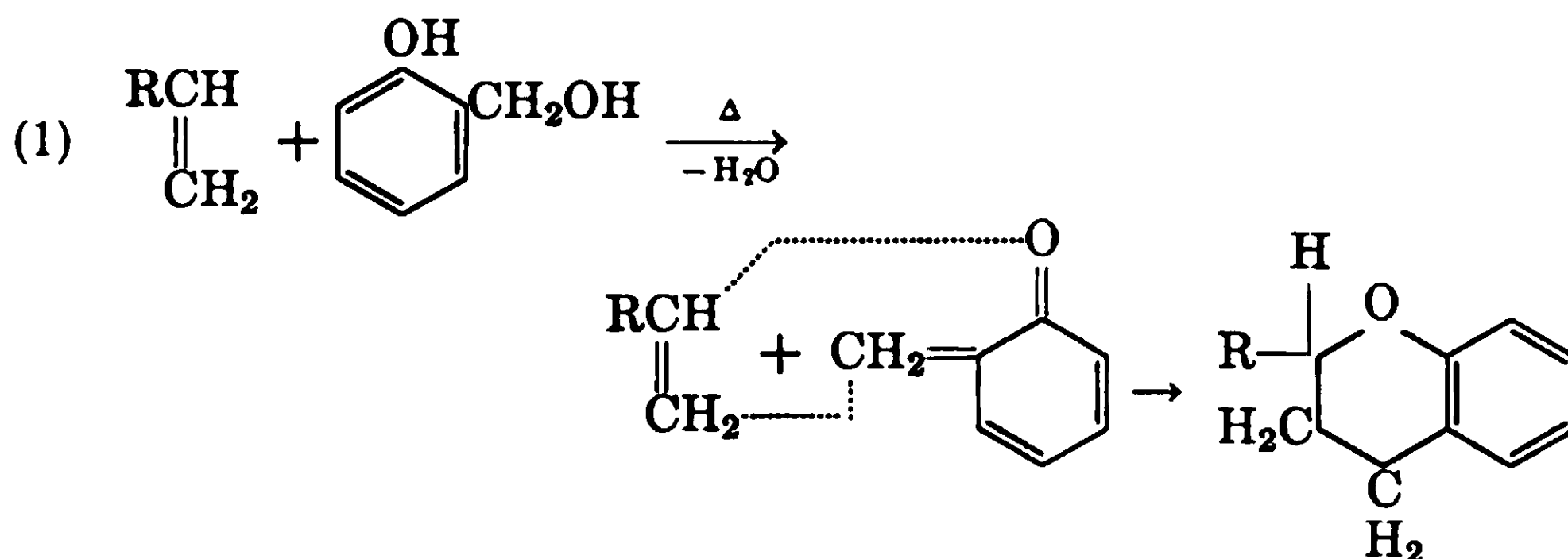
In the early thirties Hönel⁹⁻¹⁸ discovered and developed the so-called "heat-hardenable" oil-soluble resins. They were prepared by condensation under alkaline conditions of a substantial molar excess of formaldehyde with a phenol having a *para* substituent with 4 to 7 carbon atoms. Unlike the resins described above, which have a typical novolac resin structure, these resins were capable of undergoing further condensation by heating. They were characterized by the possession of methylol groups, or reactive derivatives thereof, which cause foaming and a great increase in viscosity when heated with drying oils at 180–250°C. The *para* substituent not only imparts oleophyllic properties to the resins but also renders the phenol difunctional in nature so that the danger from gelation by self-condensation is reduced. These resins have become very important commercially.

Although a wide variety of phenols have been investigated, only a few, such as *p*-cresol, *p*-*tert*-butyl, *p*-ethyl, *p*-*tert*-amyl, *p*-*tert*-octyl, and *p*-phenylphenol, have found commercial acceptance¹ for the preparation of heat-reactive oil-soluble resins.¹⁶⁻²⁰ These phenols produce resins of good oil solubility, superior color stability, and with approximately the correct reactivity so that they are not consumed by self-condensation before reaction with the oil is effected. Where higher functionality and superior cure are desired, blends of the above phenols with dihydroxydiphenylpropane or a trifunctional phenol have been recommended.^{21, 22}

Since their discovery a vast technology has developed dealing with the preparation of the various types of oil-soluble phenolic resins and their use with drying oils or alkyd resins. The type of varnish obtained depends not only on the amount and type of phenolic resin used but also on the choice of oil, the ratio of oil to resin, the pH of the system, and the cooking procedure. These points have been ade-

quately covered elsewhere. Our concern is with the possible interaction of the unsaturated component with the phenolic resin and the nature of the products obtained.

Before discussing the reactions of unsaturated resins or oils with phenolic resins, consideration will be given to the findings in simpler systems. It has been shown that combination occurs between phenol-aldehyde products, particularly the phenol alcohols, and many simple ethylenically unsaturated compounds.²³ The reaction of *o*-phenol alcohols at high temperatures with unsaturates leads to the formation of chromans. It has been suggested²³⁻²⁵ that the phenol alcohol dehydrates to a quinone methide which then adds to the unsaturated compound by means of Diels-Alder type of addition, equation 1. A

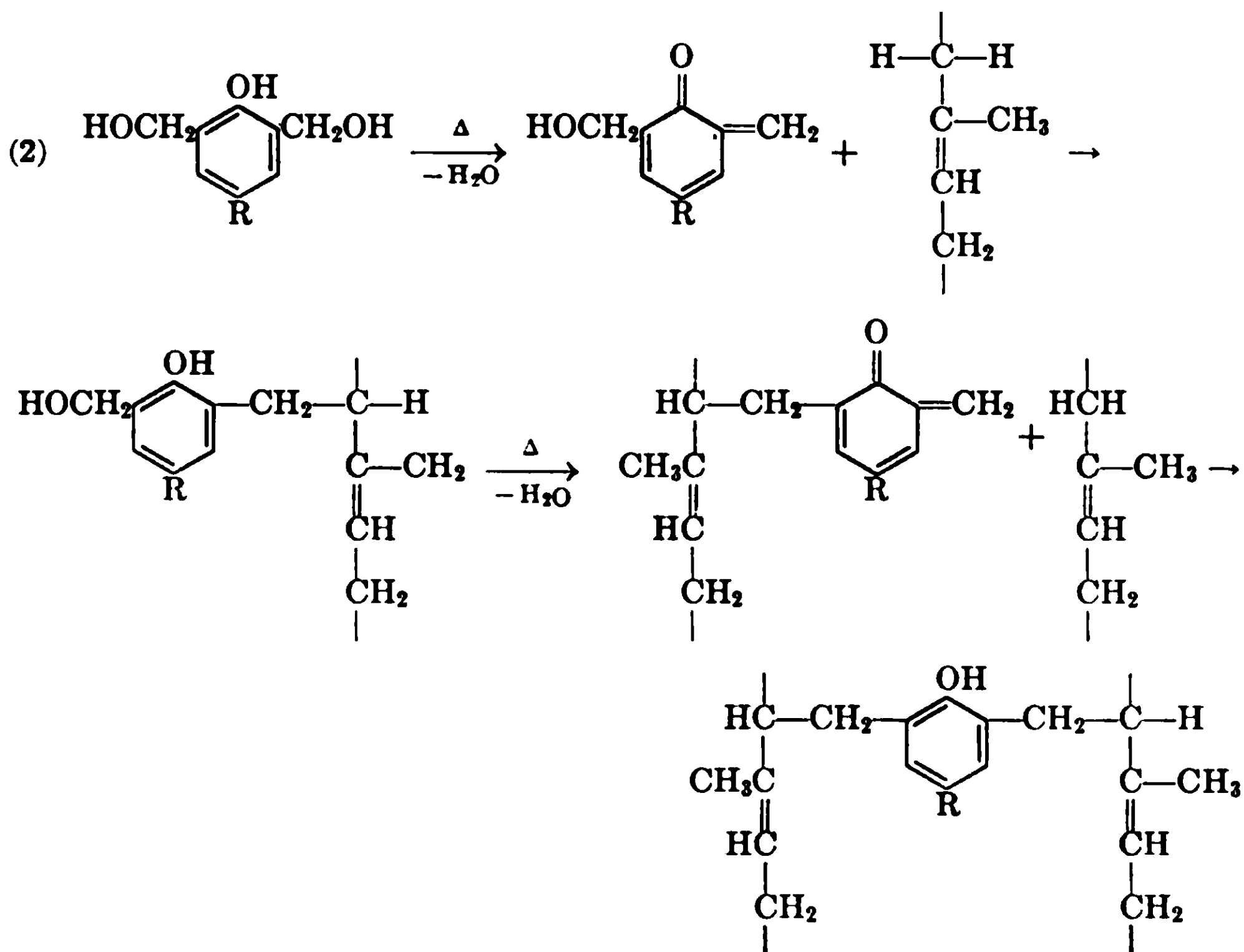


number of studies have been made of the reaction using a variety of phenol alcohols and unsaturates. Included among the phenol alcohols have been 2-hydroxy-5-methylbenzyl alcohol,²³ *p*-cresol dialcohol,²³ 2-hydroxy-3-methyl-5-*tert*-butylbenzyl alcohol,²³ 3,5-dimethyl-6-hydroxybenzyl alcohol,²³ 3-*tert*-butyl-5-methyl-6-hydroxybenzyl alcohol,²³ 3-cyclohexyl-5-methyl-6-hydroxybenzyl alcohol,²³ and saligenin.²³⁻²⁴ Bis-(3,5-dimethyl-6-hydroxybenzyl) ether²³ and bis-(2-hydroxy-3-methyl-5-*tert*-butylbenzyl) ether²⁶ also react with unsaturates. An equally impressive list of unsaturates has been investigated, e.g., styrene,²³ indene,²³ terpineol,²³ dihydromyrcene,²⁴ 1-methylcyclohexene,²⁴ dialkyl maleates,²³ allyl caproate,²³ methyl oleate,^{23, 27} and oleic,^{23, 23, 27} crotonic,²³ and abietic acids.²³ In each example a particular substituted chroman was claimed.

Because of space requirements *p*-hydroxybenzyl alcohols are not capable of chroman formation. This means that if reaction occurs between *para* phenol alcohols and unsaturated compounds a different mechanism must be involved. One of the earliest explanations for a reaction between phenol alcohols and unsaturated compounds not involving chroman formation came from Van der Meer,²³⁻²⁵ who found

that the dialcohols of both *ortho*- and *para*-substituted phenols function as curing agents for rubber. See also the work of Wildschut.^{84,88}

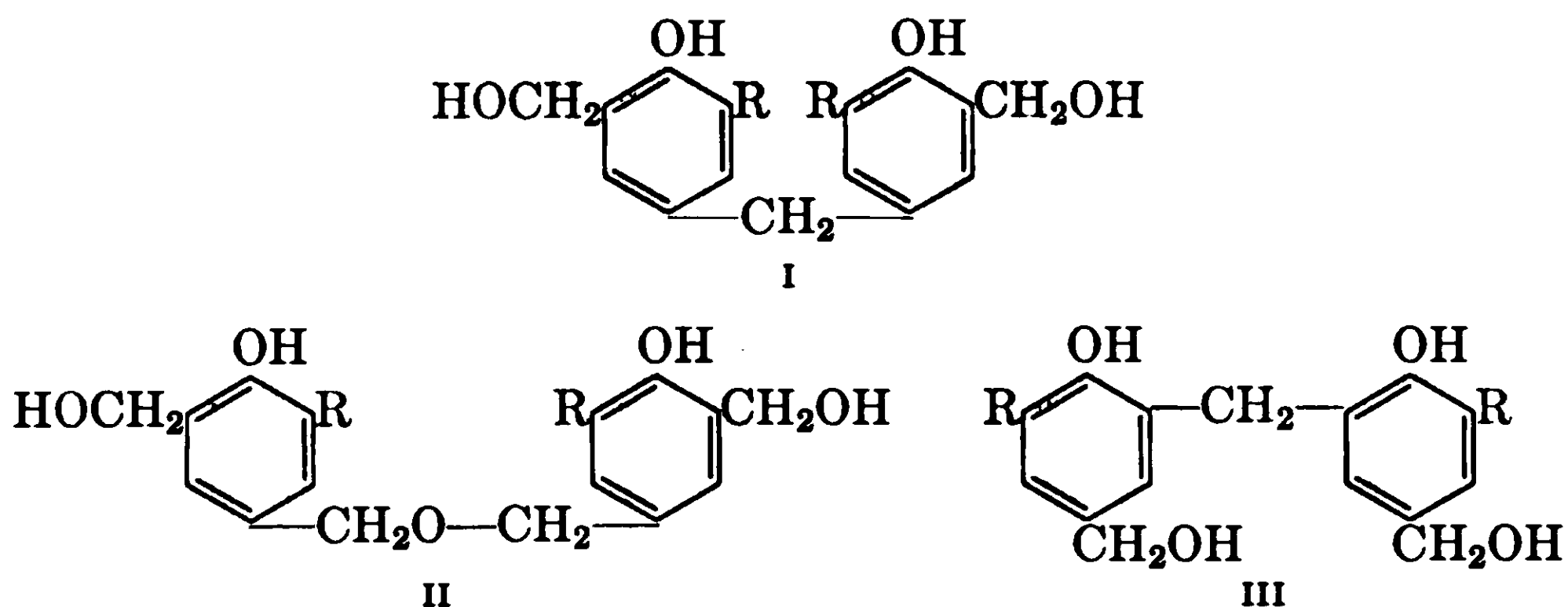
It was proposed that vulcanization occurred by attack of a quinone methide, formed by dehydration of the phenol alcohol, at an α -methylene of the rubber hydrocarbon, reaction 2. The reaction is shown for



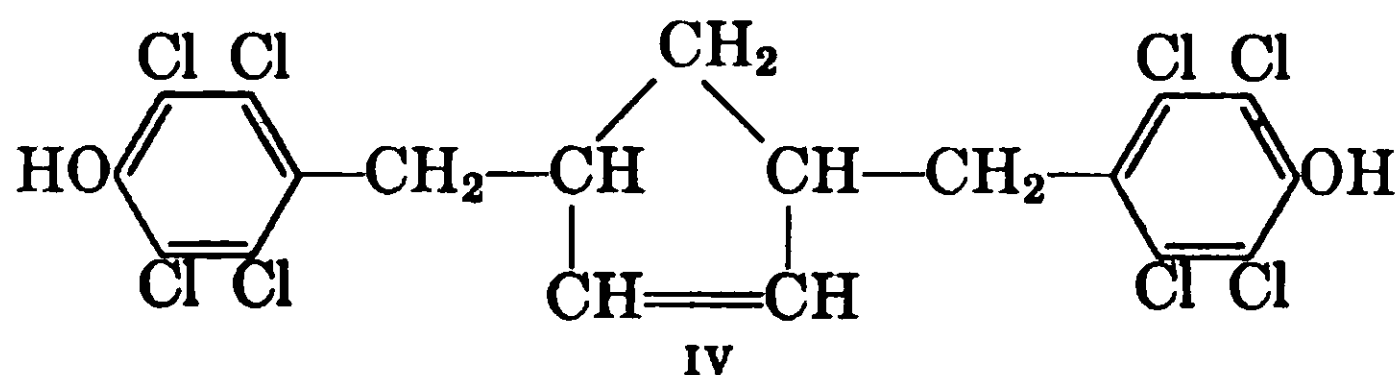
an *o,o'*-dialcohol, but according to Van der Meer it also may occur with an *o,p'*-dialcohol. *o*-Cresol dialcohol required a temperature of 200°C. for vulcanization as compared to 150°C. for *p*-cresol dialcohol. The difference in reactivity was attributed to the greater ease of formation of a quinone methide from an *o*-methylophenol. Chloromethylphenols also functioned as vulcanizing agents for rubber.

Van der Meer's mechanism has been a subject for considerable discussion. As yet conclusive evidence either proving or disproving it has not been presented. It is well known that phenol alcohols may undergo self-condensation at the temperatures used during vulcanization. Since *p*-methylophenol groups are susceptible to condensation reactions there would be a strong tendency for an *o,p'*-dialcohol to form a methylene or dibenzyl ether derivative such as I or II. Compounds of this type would then be capable of reaction with the rubber through the *o*-methylophenol groups solely by chroman formation. Van der Meer⁸¹

discounts this type of reaction since he has shown that at 200–220°C. the dinuclear dialcohol III, which has only *p*-methylol groups, is capable of vulcanizing rubber. Lilley³⁶ and Bevan³⁷ also have suggested that phenol alcohols may react with oils at the methylene group α to a double bond.



Pummerer³⁸ has reported an interesting reaction which may have a bearing on the mechanism by which *p*-methylolphenols react with compounds having conjugated double bonds. The dehydro form of tetrachloro-*p*-cresol, produced by oxidation of tetrachloro-*p*-cresol, readily adds to cyclopentadiene, 2,3-dimethylbutadiene, and other dienes. The product from cyclopentadiene IV is formed by 1,4-addition of the cresol compound to the diene. Pummerer thinks that the dehydro form of *p*-cresol should be viewed as a diradical rather than as a quinone methide. But, regardless of the active form assumed for the intermediate, the reaction of dehydro-*p*-cresol with dienes suggests that *p*-methylolphenols may react with dienes, after dehydration to a *p*-quinone methide or to a diradical, in a similar manner. Such a reaction has, indeed, been found. Lilley³⁹ has reported that quinone methides add to piperylene, myrcene, 1,4-diphenylbutadiene, and chloroprene. The reactions apparently occur by 1,4-addition.



On leaving the simple unsaturates and considering the unsaturated fatty oils, natural resins, rosin, etc., it is not surprising that the question of coreaction with a phenolic resin has been so much debated

in the literature.^{2, 4, 5, 12-14, 19, 22, 25, 28, 55 40-55} In such complex systems it is difficult to demonstrate coreaction since both the unsaturated compound and the phenolic resin polymerize independently. As both reactants are complex mixtures often of a relatively high molecular weight, the more common means for separating the components into pure fractions, such as by fractional distillation or crystallization, are of little value. Chromatography has been useful in certain instances, however.^{26, 42}

Measurements on the water evolved indicates the progress of the reaction of the phenolic component but tells nothing of the extent of coreaction since the amount of water evolved is the same when the phenolic resin condenses with itself or with an unsaturate. The data on water evolution have at times been used incorrectly as an argument against reaction between a phenolic resin and an unsaturated compound.^{54, 55}

Among the early workers Dold⁵⁵ thought that the solubilization of a phenolic resin by heating with rosin occurred simply by a process of colloidal dispersion. Buser⁵⁶ held similar views. Although it has not been possible to explain the properties of the products obtained by assuming a simple dispersion of the resin in an oil, the importance of physical processes in systems where particles of colloidal size may be involved should not be dismissed. In more recent times some type of chemical reaction between the oil and unsaturated compound has become generally accepted. However, many consider that the exact nature and the relative importance of the reactions involved in cooking a phenolic resin with an unsaturated oil or resin are still uncertain.

Hilditch and Smith⁵⁷ were among the first to challenge the theory of simple dispersion. They heated *p*-cresol dialcohol with various oils and studied the products obtained. No reaction with paraffins or with methyl esters of simple saturated or monounsaturated acids were found. (The reaction of monounsaturated acids was later proved.) Some reaction was observed with all the polyunsaturated esters tested, and the reaction appeared to proceed most readily with those esters possessing conjugated double bonds. Since then a great amount of data has been collected, many of which indicate that there is indeed a chemical interaction between the oil and resin. The arguments for reaction of one type or another may be summarized under the following headings:

1. When oil and resin are heated together the increase in viscosity occurs at a rate far in excess of that found when either material is heated alone.^{40, 41, 47-49, 55}

2. The loss of formaldehyde, which frequently accompanies self-

condensation of a phenolic resin, is reduced or eliminated when the resin is heated with oil.^{7, 26, 27, 41, 50, 54}

3. Well-defined compounds, chromans and chromones, have been formed by reaction of simple unsaturates, including oleic acid and methyl oleate, with phenol alcohols.^{26, 28, 27}

4. Color formation on heating of resin is minimized by the presence of oil. Products of lightest color are formed with oils of greatest unsaturation.⁷

5. The rate of disappearance of double bonds of the oil is accelerated by the addition of phenolic resin.^{18, 41, 42, 44, 55-59}

6. A decrease in hydroxyl content and total active hydrogens of the phenolic resin occurs on heating with the oil.^{26, 27, 42, 51}

7. The increase in the refractive index of the mixture is above that added by the phenolic resin.¹⁸

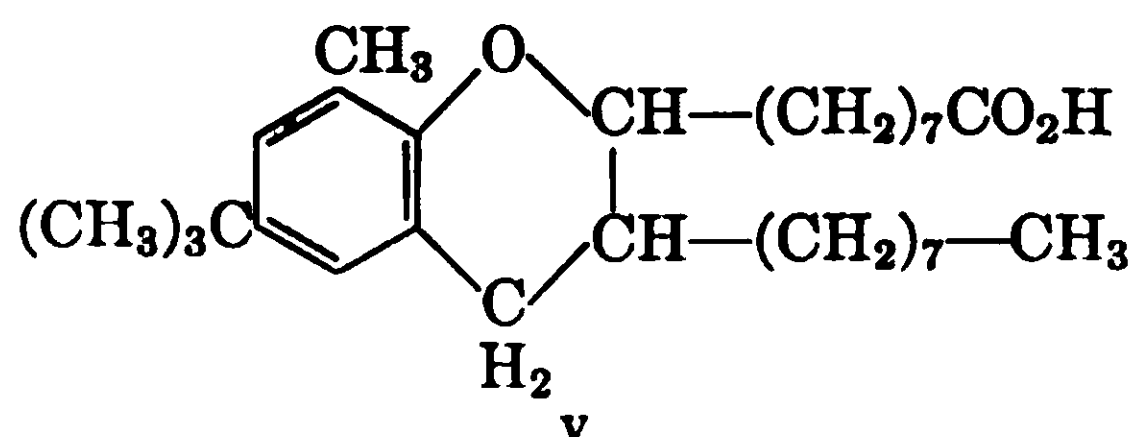
8. Heating the oil and resin separately does not improve compatibility. Heating together does.^{7, 51}

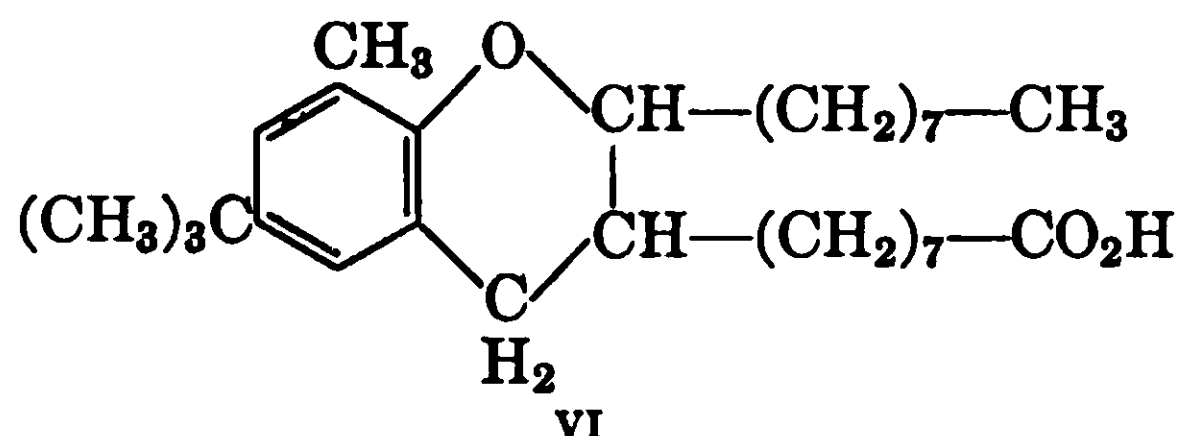
9. Gelation is sensitive to the methylol content of the phenolic resin.^{40, 41, 54, 58}

10. The reactivity of the oil with the phenolic resin changes with the degree of unsaturation of the oil.^{5, 41, 46, 57, 58}

As might be expected, many different reactions have been suggested to explain the results outlined above. From among the many considered, chroman formation is supported by the greatest amount of experimental evidence. The most convincing evidence is the unequivocal proof of chroman formation with simple unsaturated compounds. Not only highly reactive unsaturated compounds such as styrene but also compounds such as oleic acid and methyl oleate have been used in these studies. The esters of oleic acid are certainly among the least reactive esters to be found in drying oils yet they form chromans.

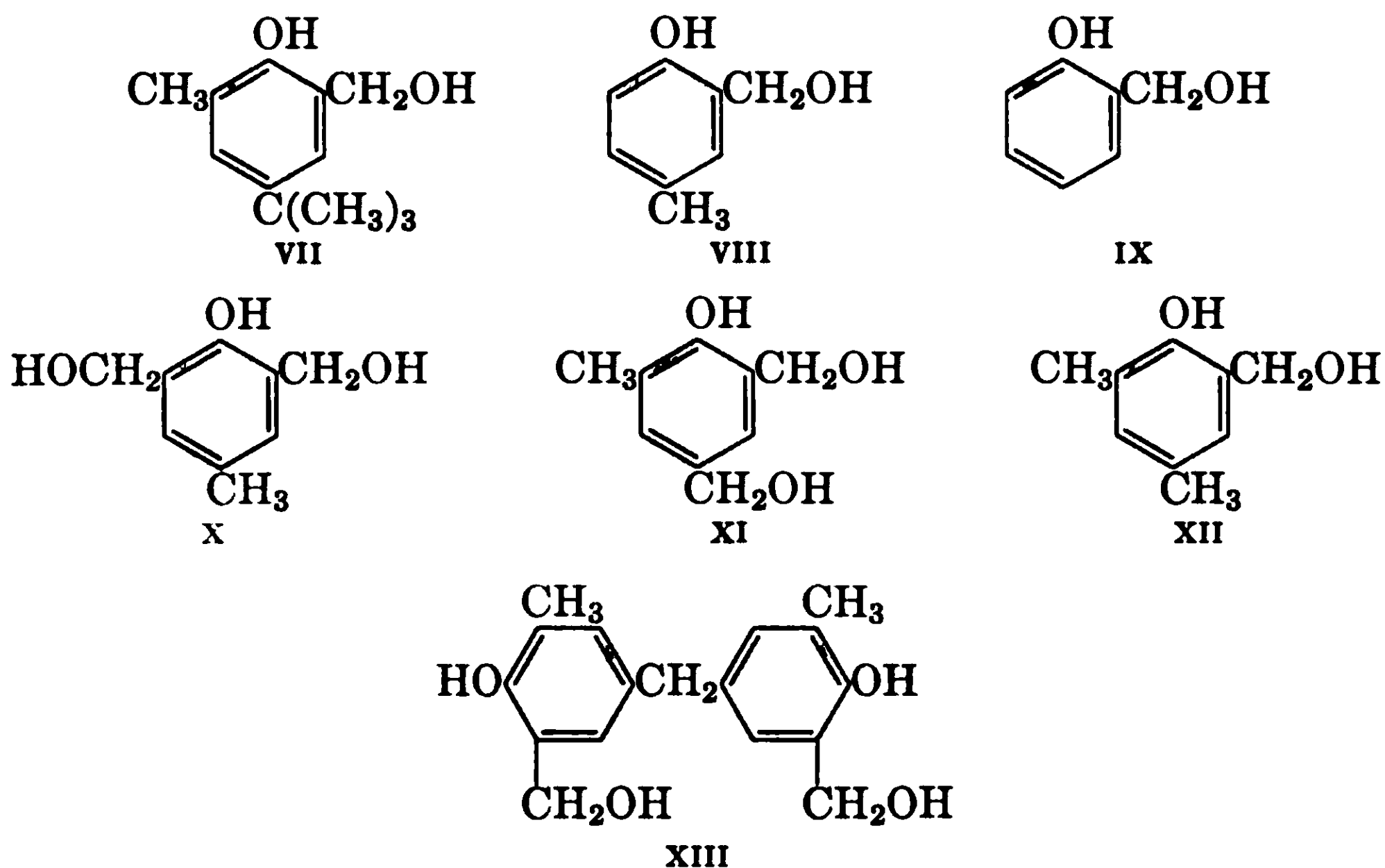
Sprengling^{26, 27} has made a detailed study of the reaction of selected phenol alcohols with oleic acid and with methyl oleate. The first publication by Sprengling was concerned with the reaction of 2-methyl-4-*tert*-butyl-6-methylolphenol with the above-named unsaturated compounds. During 3-4 hours' heating at 180°C. almost exactly 1 mole of water but no formaldehyde was evolved. By means of chromatography a product was separated having a chroman structure, V or VI.





A choice could not be made between these structures, and probably both compounds were formed. Under the conditions used for the reaction between 35 and 45 mole per cent of the phenol alcohol reacted to form a chroman derivative. The rest of the phenol alcohol went into the formation of polymers presumably via an intermediate quinone methide. The polymer had a molecular weight corresponding to three to four methylolphenol units and a very low hydroxyl content, indicating that it was probably a polymeric quinone methide.

In subsequent studies Sprengling investigated the reaction of the phenol alcohols VII to XIII with oleic acid.²⁷ The mole per cent of



each phenol alcohol that was converted to a chroman derivative is given in Table I. On the basis of the results with these phenol alcohols Sprengling made a number of interesting observations which may be summarized as follows:

1. With blocked monomethylolphenols, chroman formation is furthered by heavier alkyl groups.
2. Chroman formation is an important reaction even when free nuclear positions or a second methylol group is available.

Table I

Phenol Alcohol	Mole Per Cent Converted to Chroman
2-Methylol-4- <i>t</i> -butyl-6-methylphenol (VII)	50-51
2-Methylol-4-methylphenol (VIII)	27-29
2-Methylolphenol (IX)	16-20
2,6-Dimethylol-4-methylphenol (X)	30
2,4-Dimethylol-6-methylphenol (XI)	24
2-Methylol-4,6-dimethylphenol (XII)	35
3,3'-Dimethylol-4,4'-dihydroxy-5,5'-dimethyldi- phenylmethane (XIII)	—

3. When a blocked *o*-monomethylolphenol, such as 2-methylol-4,6-dimethylphenol, is heated with oleic acid no formaldehyde and 1 mole of water is evolved per mole of phenol alcohol. The products contain few if any free hydroxyl groups. This indicates that essentially all the methylolphenol has reacted through a quinone methide to form either a chroman derivative or quinone methide polymer.

4. In oleic acid, monomethylolphenols with free reactive ring positions evolve a mole of water and no formaldehyde. This means that there can be no permanent dibenzyl ether formation. However, there are hydroxyl groups in the product, indicating the direct formation of dihydroxydiphenylmethanes. The direct formation of dihydroxydiphenylmethanes, chromans, and quinone methide polymers appears to be roughly competitive reactions.

5. In oleic acid, dimethylolphenols evolve some formaldehyde, 0.04–0.08 mole per mole of methylol group, and approximately a mole of water. The product contains almost no free hydroxyl groups but has a saponification value close to 1 for each mole of dialcohol. This indicates that one of the methylol groups has formed a quinone methide which has reacted to form chromans and some quinone methide polymer. The other methylol group is largely esterified by the oleic acid, although a small part may form dihydroxydiphenylmethanes.

6. In methyl oleate or in linseed oil the above monomethylolphenols tend to form more dibenzyl ether and somewhat less chroman.

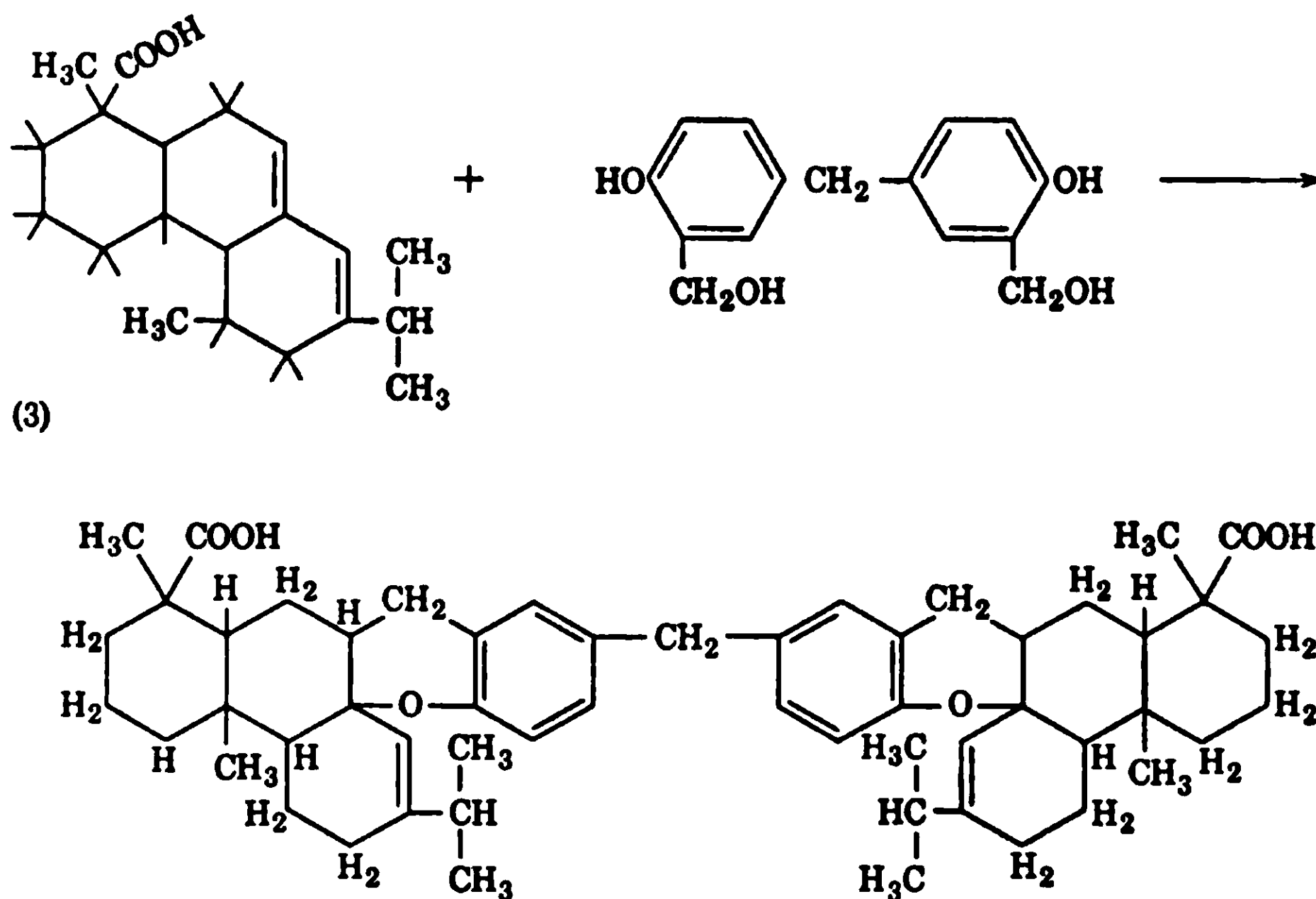
7. In an inert medium, such as transformer oil, the phenol alcohols lose formaldehyde and form insoluble, friable resins.

The results obtained by Sprengling show conclusively that chroman formation is an important reaction of oils with phenol alcohols, even with those of low reactivity. They also point up a number of the side reactions that may occur.

The formation of a chroman from a phenol alcohol and an unsatu-

rated compound requires participation of the phenolic hydroxyl group. A further indication that the phenolic hydroxyl group is involved in oil reactivity is the observation that blocking or absence of a phenolic hydroxyl group prevents reaction with an oil.^{23, 29, 50, 52} On the other hand blocking of a methylol group causes no such loss of reactivity. This is explained by the fact that the postulated quinone methide intermediate may be formed from the functional derivatives of the methylol group, such as from the alkoxymethylphenols, acyloxymethylphenols, dihydroxydibenzyl ethers, halomethylphenols, and benzodioxans.^{28, 28} This point is important, as dihydroxydibenzyl ethers, in particular, are often formed during heat bodying of the heat-reactive resins prepared from alkyl phenols.

Castle⁵¹ and Pritchett⁵² report that phenol may be split from the end of the chain of an oil-soluble novolac resin during cooking with an oil. They suggest that by this means a quinone methide might be formed at the end of the chain of a so-called non-heat-reactive resin. If formed, the quinone methide should be capable of reaction with an oil.

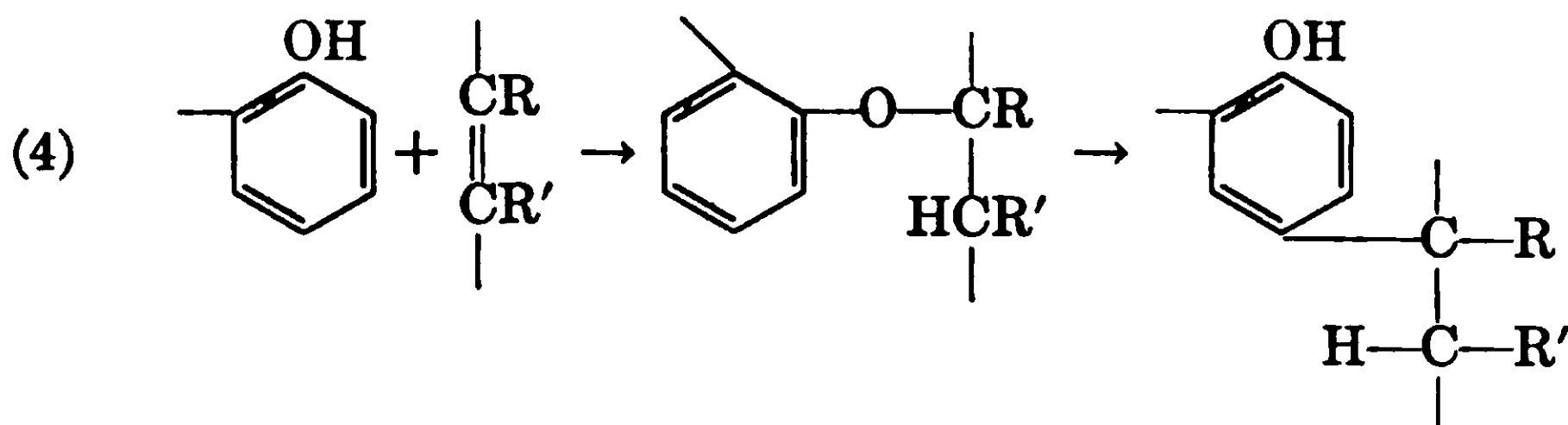


The solubilization of phenolic resins by heating with rosin also has been attributed to chroman formation. Rosin is composed of several unsaturated acids, of which abietic is the most important. Hultsch⁵ has given a probable structure for the dichroman from 3,3'-dimethylol-4,4'-dihydroxydiphenylmethane and abietic acid, equation 3. Greth⁷

has proposed similar structures for the products except that dibenzyl ether linkages between the phenolic residues are favored over methylene bridges.

Besides chroman formation, ester exchange may occur between the glycerides of the oil and the hydroxyls of the phenolic resin.^{41, 50, 55, 55-55} According to Charlton and Perrins,⁵⁰ such a reaction is strongly indicated with low-molecular-weight resins. Powers⁴⁸ also considers this reaction to be important. Nevertheless, it is doubtful that ester exchange is the major reaction; otherwise saturated and unsaturated esters would behave roughly the same, which is not found experimentally. Sprengling²⁷ has shown, as reported earlier, that fatty acids, if used in place of esters, may esterify the methylol groups of a phenol alcohol.

The addition of a phenol to the double bond of an unsaturated compound to form a phenyl ether is a well-known reaction. The ether normally rearranges to a substituted phenol, particularly when in contact with an acidic or Friedel-Crafts catalyst. This reaction is used extensively for the alkylation of phenols with simple unsaturates and has also been employed with unsaturated oils.⁵⁶ Similar reactions might occur when oils and phenolic resins are brought together at high temperatures (equation 4). This possibility has been discussed by Castle.⁵¹



From a practical point of view the oil or natural resin-phenolic condensates can be prepared in several ways.^{15, 57-75} The phenolic resin can be prepared separately and then reacted with the unsaturate, or the phenolic resin can be prepared in the presence of the unsaturated compound. In the latter procedure the phenol and formaldehyde and unsaturated product are mixed and heated until the major part of the formaldehyde is consumed; then the water is removed and the temperature raised to 180–250°C., where the reaction is completed.⁷⁴ In general a phenolic resin of low or moderate reactivity is most suitable; otherwise the phenolic resin will be consumed by self-condensation before appreciable reaction with the unsaturated product has occurred. Even at best it appears certain that some self-condensation of both the

unsaturated material and the phenolic resin takes place during a normal cooking operation. The extent of such self-condensation is affected by the compatibility of the reactants and, as mentioned earlier, by the degree of unsaturation and the amount of conjugation in the unsaturated material. Self-condensation of the phenolic resin is evident from the loss of formaldehyde which occurs during the cooking.^{2, 5} The degree of condensation of the phenolic resin before addition of rosin affects the extent of coreaction and also the melting point of the products. A low-molecular-weight condensate may increase the melting point of the product 40–50°C.; a highly condensed resin will cause only a 12–14°C. rise in melting point.⁴⁹ The ideal temperature for reaction appears to be in the range from 180° to 230°C.

REFERENCES FOR CHAPTER 8

- ¹ T. S. Carswell, *Phenoplasts*, Interscience Publishers, New York, 1947, pp. 204–213.
- ² K. Hultzsich, *Kunststoffe*, **37**, 43–45 (1947).
- ³ K. Hultzsich, *Angew. Chem.*, **A60**, 179–184 (1948).
- ⁴ H. von Euler, *Angew. Chem.*, **54**, 458 (1941).
- ⁵ K. Hultzsich, *Chemie der Phenolhärze*, Springer-Verlag, Berlin, 1950, pp. 78, 156–165.
- ⁶ L. Berend, Ger. pats. 254,411; 281,939; 289,968 (1910), U. S. pat. 1,191,390 (1916).
- ⁷ A. Greth, *Kunststoffe*, **31**, 345 (1941).
- ⁸ V. H. Turkington and W. H. Butler, U. S. pat. 2,017,877 (1935).
- ⁹ H. Hönel, Brit. pat. 417,122 (1934).
- ¹⁰ H. Hönel, U. S. pats. 1,996,169 (1935); 1,996,170 (1935).
- ¹¹ H. Hönel, *J. Oil & Colour Chemists' Assoc.*, **21**, 247–276 (1938).
- ¹² H. Hönel, *Fette u. Seifen*, **45**, 636–682 (1938).
- ¹³ H. Hönel, *Fette u. Seifen*, **46**, 29 (1939).
- ¹⁴ H. Hönel, *Oil Colour Trades J.*, **93**, 593 (1938).
- ¹⁵ H. Hönel, U. S. pat. 1,870,453 (1932).
- ¹⁶ V. H. Turkington and I. Allen, Div. Paint, Varnish, and Plastics Chem., 101st meeting of American Chemical Society, St. Louis, Mo., 1941.
- ¹⁷ V. H. Turkington and I. Allen, *Ind. Eng. Chem.*, **33**, 966–977 (1941).
- ¹⁸ V. H. Turkington, R. C. Shuey, and L. Scheckter, *Ind. Eng. Chem.*, **30**, 984 (1938).
- ¹⁹ T. N. Mehta, *Paint Oil Chem. Rev.*, **107**, 9–12, 46 (May 4); 9, 20–25 (July 27); 12–14 (Aug. 10); 14–16 (Aug. 24, 1944).
- ²⁰ T. N. Mehta, *Paint Oil Chem. Rev.*, **108**, 18, 22–24 (Jan. 11, 1945).
- ²¹ R. H. Runk, *Ind. Eng. Chem.*, **42**, 2110–2114 (1950).
- ²² P. O. Powers, *Ind. Eng. Chem.*, **36**, 1008–1012 (1944).
- ²³ K. Hultzsich, *J. prakt. Chem.*, **158**, 275–294 (1941).
- ²⁴ J. I. Cunneen, E. H. Farmer, and H. P. Koch, *J. Chem. Soc.*, **1943**, 472–476.
- ²⁵ K. Hultzsich, *Ber.*, **74B**, 898–904 (1941).

- ²⁵ G. R. Sprengling, Preprint *Bull., Div. Paint, Varnish, and Plastics Chem.*, American Chemical Society Meeting, September 1950, Chicago, pp. 78-83, *J. Am. Chem. Soc.*, **74**, 2937 (1952).
- ²⁷ G. R. Sprengling, private communication.
- ²⁸ S. Van der Meer, *Papers* 47, 48, Rubber-Stichting, Delft, Holland, 1944.
- ²⁹ S. Van der Meer, *Paper* 44, Rubber Stichting, Delft, Holland, 1946.
- ³⁰ S. Van der Meer, *Rubber Chem. and Technol.*, **18**, 853-873 (1945).
- ³¹ S. Van der Meer, *Kunststoffe*, **37**, 41 (1947).
- ³² S. Van der Meer, *Rec. trav. chim.*, **63**, 147-156 (1944).
- ³³ S. Van der Meer, *Rec. trav. chim.*, **63**, 157-169 (1944).
- ³⁴ A. J. Wildschut, *Paper* 36, Rubber-Stichting, Delft, Holland, 1943.
- ³⁵ A. J. Wildschut, *Rubber Chem. and Technol.*, **19**, 86-99 (1946).
- ³⁶ H. S. Lilley, *Paint Technol.*, **7**, 58-59, 77-78, 92, 94 (1942).
- ³⁷ E. A. Bevan, *Varnish Making*, Oil and Colour Chemists' Assoc., Chemical Publishing Co., New York, 1939, p. 114.
- ³⁸ R. Pummerer, G. Schmidutz, and H. Seifert, *Ber.*, **85**, 535 (1952).
- ³⁹ H. S. Lilley, *J. Oil & Colour Chemists' Assoc.*, **26**, 88-95 (1943).
- ⁴⁰ H. S. Lilley and D. W. J. Osmond, *Paint Technol.*, **13**, 217-224 (1948).
- ⁴¹ H. S. Lilley, *Varnish Making*, Oil and Colour Chemists' Assoc., Chemical Publishing Co., New York, 1939, pp. 107-121.
- ⁴² H. S. Lilley, *Paint Technol.*, **8**, 189-191 (1943).
- ⁴³ H. S. Lilley, *Paint Technol.*, **10**, 133-137 (1945).
- ⁴⁴ R. J. R. Singer, *Kunststoffe*, **33**, 233 (1943).
- ⁴⁵ H. W. Rudd, *Paint Manuf.*, **16**, No. 3, 72-79, No. 4 123-126 (1947).
- ⁴⁶ F. J. Siddle, *Varnish Making*, Oil and Colour Chemists' Assoc., Chemical Publishing Co., New York, 1940, p. 91.
- ⁴⁷ P. O. Powers, Preprint *Bull., Div. Paint, Varnish, and Plastics Chem.*, American Chemical Society Meeting, September, 1950, pp. 84-92.
- ⁴⁸ P. O. Powers, *Ind. Eng. Chem.*, **42**, 146-150 (1950).
- ⁴⁹ P. O. Powers, *Ind. Eng. Chem.*, **43**, 1770-1774 (1951).
- ⁵⁰ W. Charlton and L. E. Perrins, *J. Oil & Colour Chemists' Assoc.*, **30**, No. 324, 185 (1947).
- ⁵¹ R. Castle, *Paint, Oil, Colour J.*, **120**, 493-495 (August, 1951).
- ⁵² H. S. Lilley and D. W. J. Osmond, *Kunststoffe*, **38**, 112 (1948).
- ⁵³ C. P. A. Kappelmeier and W. R. van Goor, *Verfkroniek*, **16**, 68 (1943).
- ⁵⁴ H. S. Lilley, *Paint Technol.*, **11**, 179-180 (1946).
- ⁵⁵ K. H. Dold, *Schweiz. Arch. angew. Wiss. u. Tech.*, **3**, 325 (1937).
- ⁵⁶ K. Buser, *Farbenztg.*, **45**, 148 (1940).
- ⁵⁷ T. P. Hilditch and C. J. Smith, *J. Soc. Chem. Ind.*, **54**, 111-115T (1935).
- ⁵⁸ H. S. Lilley, *Varnish Making*, Oil and Colour Chemists' Assoc., Chemical Publishing Co., New York, 1940, pp. 113-120.
- ⁵⁹ R. J. R. Singer, *Kem. Maanedssblad*, **23**, 49-61 (1942).
- ⁶⁰ R. Shuey, *Ind. Eng. Chem.*, **32**, 921 (1940).
- ⁶¹ R. F. Bowles, *Chemistry & Industry*, **60**, 866 (1941).
- ⁶² E. G. K. Pritchett, *Chemistry & Industry*, 1949, 295-299.
- ⁶³ K. Pistor, *Z. angew. Chem.*, **38**, 831, 1118 (1925).
- ⁶⁴ J. J. Sleightholme, *Varnish Making*, Oil and Colour Chemists' Assoc., Chemical Publishing Co., New York, 1940, p. 86.
- ⁶⁵ H. H. Morgan, *J. Oil & Colour Chemists Assoc.*, **15**, 106 (1932).
- ⁶⁶ F. J. Hermann, Dutch pat. 66,225 (1950).

⁶⁷ J. J. Mattiello, *Protective and Decorative Coatings*, Vol. 1, John Wiley & Sons, New York, 1941.

⁶⁸ V. H. Turkington, U. S. pat. 2,242,489 (1941).

⁶⁹ R. N. Shreve and B. Golding, *Ind. Eng. Chem.*, **43**, 134-141 (1951).

⁷⁰ M. Yanagita, *Repts. Sci. Research Insti. Tokyo*, **24**, 392-397 (1948).

⁷¹ V. H. Turkington, R. C. Shuey, and W. H. Butler, *Ind. Eng. Chem.*, **23**, 791 (1931).

⁷² H. S. Lilley, *Synthetic Resins and Allied Plastics*, 2nd Ed., Oxford University Press, London, 1943, pp. 260-273.

⁷³ A. L. Brown, U. S. pats. 1,212,738 (1917); 1,632,113 (1927).

⁷⁴ N. Strafford, U. S. pat. 1,928,739 (1933).

C H A P T E R N I N E

Reactions of Phenol-Aldehyde Products

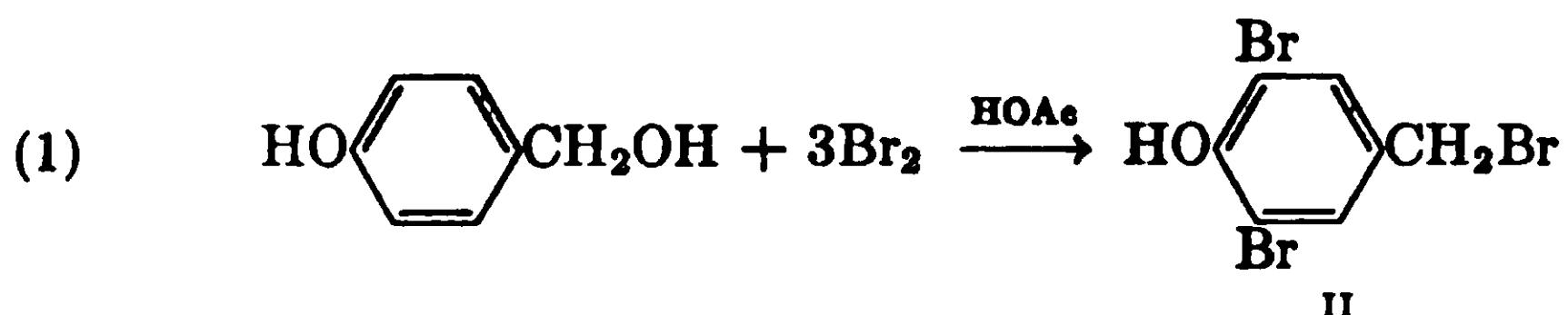
Phenol-aldehyde products are susceptible of a variety of reactions in addition to those encountered during the formation and cure of a resin. A number of the products from such reactions have found commercial application; others are under active study. Only the more important reactions will be considered here, and in general the discussion will be limited to the reactions involving the methylol (phenol alcohols and resoles) or methylene derivatives (diphenylolalkanes and novolac resins) of a phenol. The reactions will be grouped according to the reagent employed.

HALOGENS

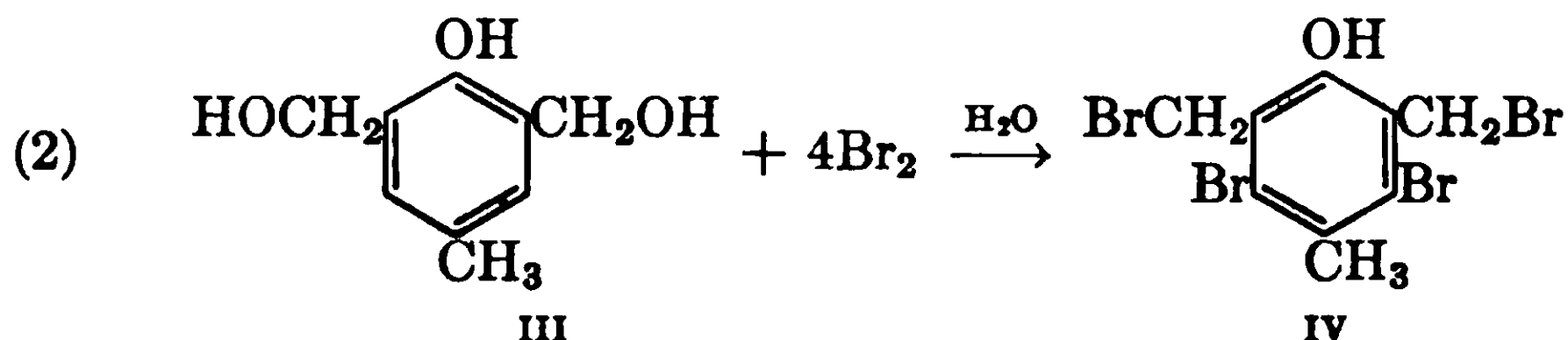
As a class the halogens are very reactive towards most phenol-aldehyde products. The products obtained depend on the reaction conditions, on the mole ratio of reactants, and to some extent on the halogen employed.

Phenol alcohols undergo three main reactions with halogens, namely, (a) conversion of methylol group to a halomethyl group, (b) replacement of the methylol group with a halogen atom, and (c) replacement of active hydrogen atoms of the phenol ring or alkyl side chain with a halogen. Selected examples of each type of reaction will be given.

Auwers¹ was one of the first to make a detailed study of the action of halogens on phenols and their derivatives. He showed that *o*- and *p*-hydroxybenzyl alcohols react with bromine in acetic acid to give the corresponding dibromobromomethylphenol II, equation 1.



In water solution the hydrogens in the *meta* position were also reactive towards bromine, equation 2.



At reflux temperature with aqueous bromine the alkyl substituent is also replaced.

Francis^{2,3} discovered that with proper control of experimental conditions reaction with a halogen could be regulated so as to either displace or leave the methylol groups intact. Sprung⁴ later made a study of the bromination of phenols with acidified bromate-bromide solution and found that saligenin absorbed essentially 3 moles of bromine; i.e., it behaved as if the methylol group were absent. Since the formation of a methylene derivative from a phenol alcohol eliminates one position on each phenol ring available for reaction with bromine, Sprung⁵ and also Nordlander,⁶ Novak and Cech,^{7,8} and Jacque⁹ have used the decrease in "bromine number" of a phenol-formaldehyde reaction mixture as a measure of the progress of the condensation reaction. (See also the work of Euler and Kispeszky.¹⁰) Oshima and Imoto¹¹ and Sprung and Gladstone¹² also used the method to follow the condensation of saligenin. The method appears reliable so long as the ratio of formaldehyde to phenol does not become too high or so long as a substituted phenol is not involved. In such instances the methylol compounds invariably absorb less than the required amount of bromine assuming that the positions occupied by methylol groups are reactive towards bromine. This was shown by Ruderman,¹³ who made a detailed study of the bromination of phenol alcohols. Trimethylolphenol gives only a very small yield of tribromophenol upon treatment with acidified bromate-bromide solution.¹⁴

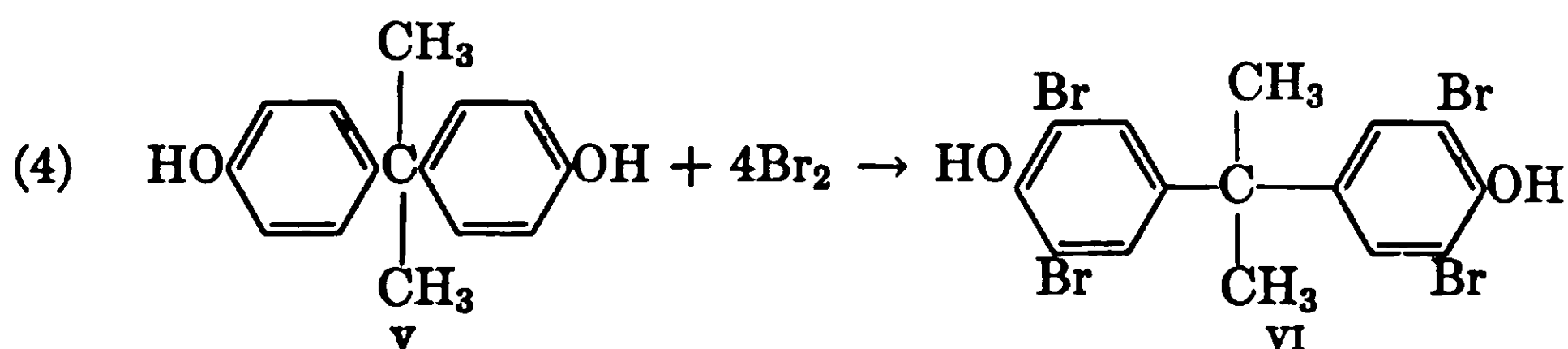
Lilley and Osmond¹⁵ have used the reaction of iodine in alkaline solution as a means for determining the methylol content of phenol-aldehyde condensation products. The method depends on the elimination of the methylol group and its oxidation to formic acid with iodine. The over-all reaction is shown in equation 3. This phase of



the reaction proceeds rapidly. The iodine may also react at free *ortho* and *para* positions of the phenol and probably in other ways as well.

The side reactions involving the iodine are difficult to correct for; this tends to make the method unreliable.^{16,17} Sprengling¹⁸ reports that the error may be as great as 30–50% with certain resole models.

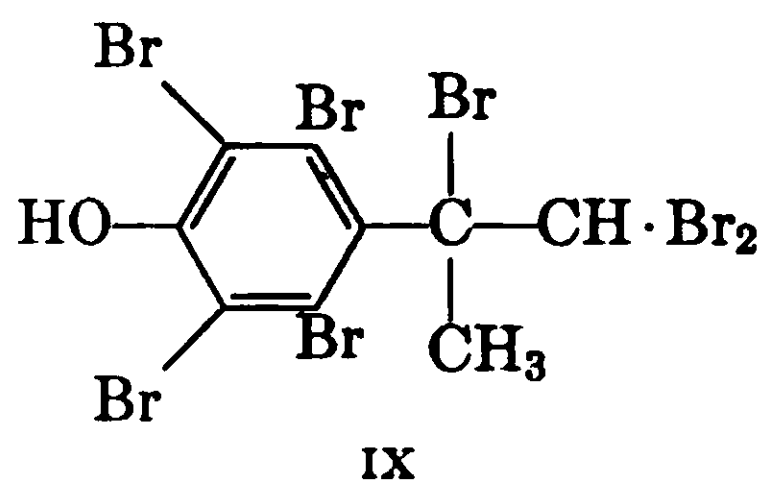
The reactions of dihydroxydiphenylalkanes with halogens are similar to those of the parent phenols except that reaction at the alkylene bridge can occur.^{19,20} Under mild conditions reaction occurs predominately at the free *ortho* and *para* positions, but even under mild conditions some attack at the alkylene bridge may be observed. The nature of the alkylene bridge as well as the location of the bridge appears to affect the extent of reaction at this point, particularly under mild conditions.^{10,21,22} As more severe reaction conditions are employed rupture of the alkylene bridge and reaction at the *meta* positions may occur. The sequence of possible reactions is illustrated by the findings of Zincke and Grueters²⁸ on dihydroxydiphenylpropane, V. Under mild conditions the tetrabromide VI resulted, equation 4.



Protracted treatment of compound VI with bromine gave a mixture of tribromophenol VII and 2,6-dibromo-4-bromopropylphenol VIII. Compound VIII could be reacted further to give the heptabromo



derivative IX.

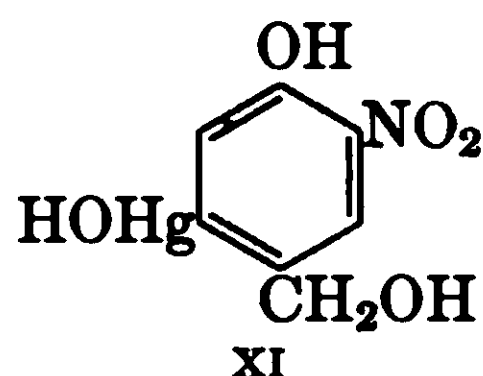
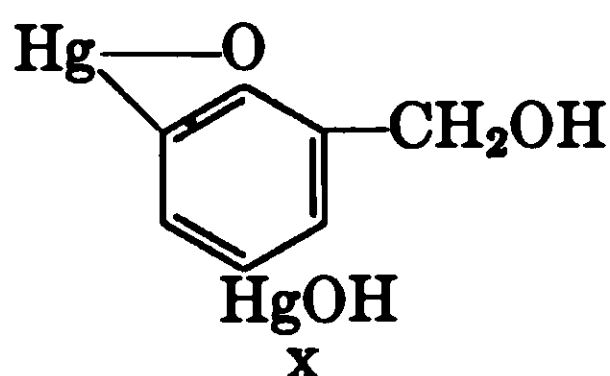


Auwers and Rietz²⁴ also showed that dihydroxydiphenylmethane could be decomposed to mononuclear products by the action of bromine. The exact course of the reaction was not determined, but it

appeared that substitution in the methylene bridge preceded decomposition.

MERCURY SALTS

Phenols, in general, are mercurated *ortho* and *para* to the phenolic hydroxyl group by heating with mercuric acetate. The dihydroxydiphenylalkanes behave like the parent phenol and need not be considered in detail.²⁵ The reactions of phenol alcohols with mercuric acetate are of more interest. Hart and Hirschfelder²⁶ reacted saligenin and 3-nitro-4-hydroxybenzyl alcohol with mercuric acetate. Saligenin formed a compound which was assigned structure X. The HgOH group was believed to be attached at the *meta* position, in the product from 2-nitro-4-methylolphenol, compound XI, since the compound



showed no tendency to lose water and form an inner anhydride. This appears to be a rather weak argument for assuming the entry of a group at a position *meta* to a phenolic hydroxyl group and at the same time *para* to a nitro group.

INORGANIC ACIDS

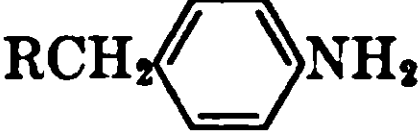
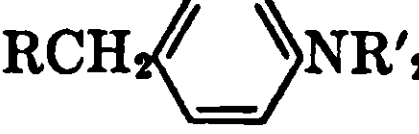
Because of the wide variations in the properties of inorganic acids, generalizations cannot be made as to their reactions with either phenol alcohols or other phenol-aldehyde products. For this reason the reactions of the more common inorganic acids will be considered separately.

Halogen Acids. From a preparative point of view the reactions of the halogen acids with phenol alcohols^{19, 27-32} and dihydroxydibenzyl ethers³²⁻³³ are the most important. The products of such a reaction are the halomethylphenols, which possess a highly reactive benzyl-type halogen atom. The preparative value of such products resides in the ease with which the halogen atom may be replaced by the action of a wide variety of reagents. Ziegler²⁷ and Zinke^{27, 33, 39} believe that the halomethylphenols are intermediates in the acid (halogen) cure of One-Stage resins, it having been demonstrated that the halomethylphenols react readily with phenols to give methylene derivatives and with phenol alcohols to give dihydroxydibenzyl ethers.

Auwers ¹⁹ made a detailed study of the preparation and reactions of halomethylphenols. The use of a solvent such as benzene, ether, or glacial acetic acid and anhydrous acid was usually beneficial in preparing the halomethyl derivatives from the phenol alcohols. It has since been found that certain phenol alcohols will also give the halomethylphenols by simply stirring with a cold concentrated aqueous solution of the acid. This type of reaction also is common with tertiary alcohols. (Also see Chapter 6.)

The variety of products that can be obtained from the halomethylphenols can be seen from an inspection of Table I. Some of the reac-

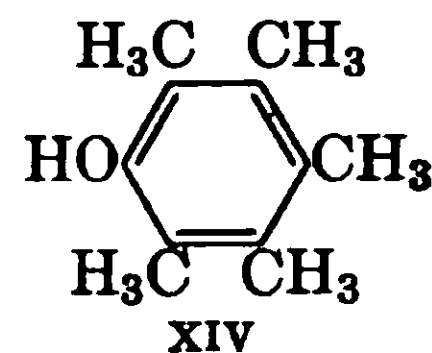
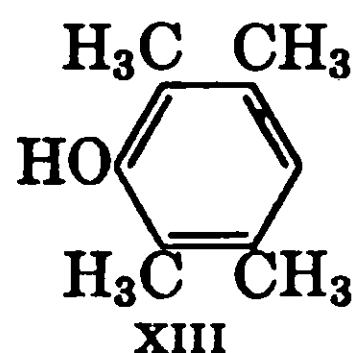
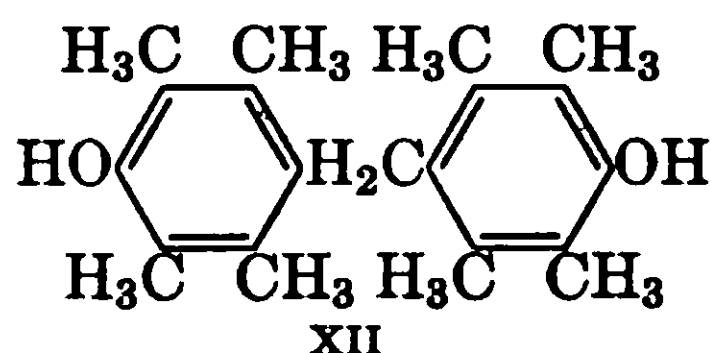
Table I. Reactions of Halomethylphenols

Reagent	Product (R = hydroxyphenyl group)	Reference
Ammonia	$(RCH_2)_3N$	49, 50
Monoalkylamine	$RCH_2NR'CH_2R$	41, 42, 49
Dialkylamine	$RCH_2NR'_2$	46, 47, 48
Aniline	RCH_2  NH_2	42, 44, 45
N,N-Dialkylaniline	RCH_2  NR'_2	18
Hydroxybenzylamines	RCH_2NHCH_2R	67
Alcohol	RCH_2OR'	18, 40-43
Phenol alcohol	RCH_2OCH_2R	56
Phenols	RCH_2R	37, 38, 61-64
Sodium hydrosulfide	RCH_2SH	44
Sodium sulfide	RCH_2SCH_2R	51, 52
Sodium cyanide	RCH_2CN	44
Sodium thiocyanate	RCH_2SCN	43, 53
Sodium acetate/water	Quinone methides	28, 44, 54, 55
	$\begin{array}{c} O \\ \\ RCH_2OCCH_3 \end{array}$	43
	$\begin{array}{c} O \\ \\ RCH_2OCC_6H_5 \end{array}$	56
Sodium benzoate/C ₆ H ₆	$RCH_2OCC_6H_5$	56
Water/acetone	RCH_2OCH_2R	33, 57
Water/AgNO ₂	RCH_2OH	58
Aldehydes	Benzodioxans	59, 60
Rubber	Vulcanizates	43, 65, 66

tions are nearly quantitative. (R represents the hydroxyphenyl or substituted hydroxyphenyl radical, and R' is an alkyl or aryl group.)

Halogen acids split dihydroxydiphenylmethanes under certain con-

ditions.^{68, 80} Buroway and Chamberlain⁷⁰ found that bis(hydroxyduryl) methane, XII, is particularly susceptible to such a reaction.



With a small amount of hydrogen chloride in acetic acid a mixture of durenol XIII and pentamethylphenol XIV was obtained. Heating the bisphenol with 1:1 hydrochloric acid in methanol gave an 83% yield of durenol but only a trace of pentamethylphenol.

Liebnitz and Nauman⁷¹ have made a detailed study of the hydrolysis of bisphenols with concentrated hydrochloric acid (sp. gr. 1.19) at 100°C. in a bomb. Many of the bisphenols gave mixtures of the original phenol along with higher alkyl-substituted phenols.

Sulfuric Acid. Phenol alcohols condense rapidly on contact with sulfuric acid to give resins whose structure has not been carefully studied. However, there is little reason to believe that the resins are formed by reactions different from those that occur when phenol alcohols are condensed in the presence of other agents. However, both sulfonation and oxidation of the resin may occur.^{61, 72, 73} The sulfonation of phenolic resins has received considerable attention, since valuable tanning agents and ion-exchange resins are prepared in this manner.⁷⁴ Products with similar properties are also obtained by the condensation of phenolsulfonic acids with formaldehyde, frequently in the presence of added phenols.⁷⁵ For ion-exchange resins trifunctional phenols are used along with the phenolsulfonic acids to provide the necessary functionality for cure. Difunctional phenols are used in preparing tanning agents since a certain degree of water solubility is required.⁷⁶

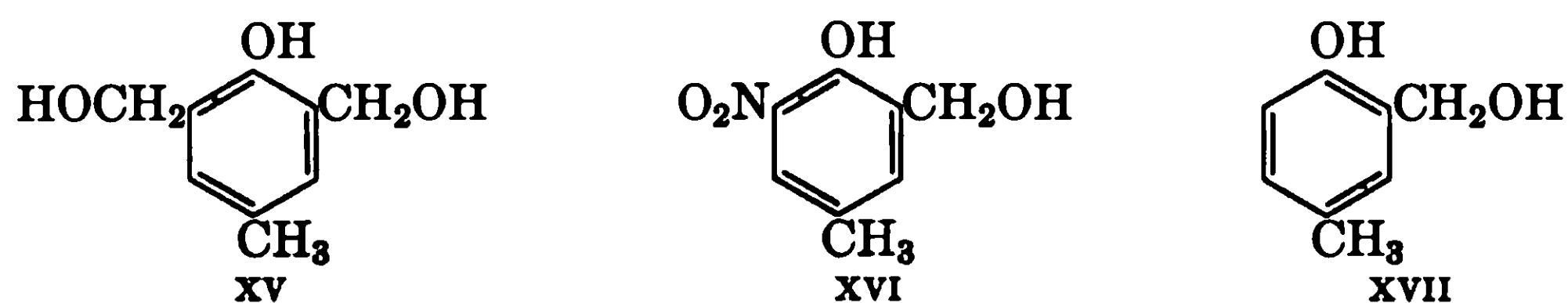
Nitric and Nitrous Acid. The products obtained by the action of nitric acid on phenolic products depends to a great extent on the concentration of the acid and on reaction conditions. This is because nitric acid may act as an oxidizing and as a nitrating agent in addition to being a source of hydrogen ions.

Under vigorous conditions essentially all phenol-aldehyde products, even cured resins, yield picric acid on treatment with nitric acid.⁷⁷ Under milder conditions nitro groups are introduced in the free *ortho* and *para* positions relative to the phenolic hydroxyl group. This reaction occurs readily with dihydroxydiphenylmethanes.^{20, 28, 78, 79} With phenol alcohols, the methylol groups may be displaced by nitro groups.

For example, 30% nitric acid reacts with *p*-cresol dialcohol to give 2,6-dinitro-4-methylphenol.⁸⁰ By careful control of reaction conditions the reaction may be regulated so that one or both of the methylol groups are replaced.⁸¹

Esterification of the methylol groups of a phenol alcohol with nitric acid has not been reported. Van der Meer⁴⁸ attempted to prepare nitrate esters by the reaction of bromomethylphenols with silver nitrite. The compounds were unstable even at low temperatures and continually evolved nitrogen oxides.

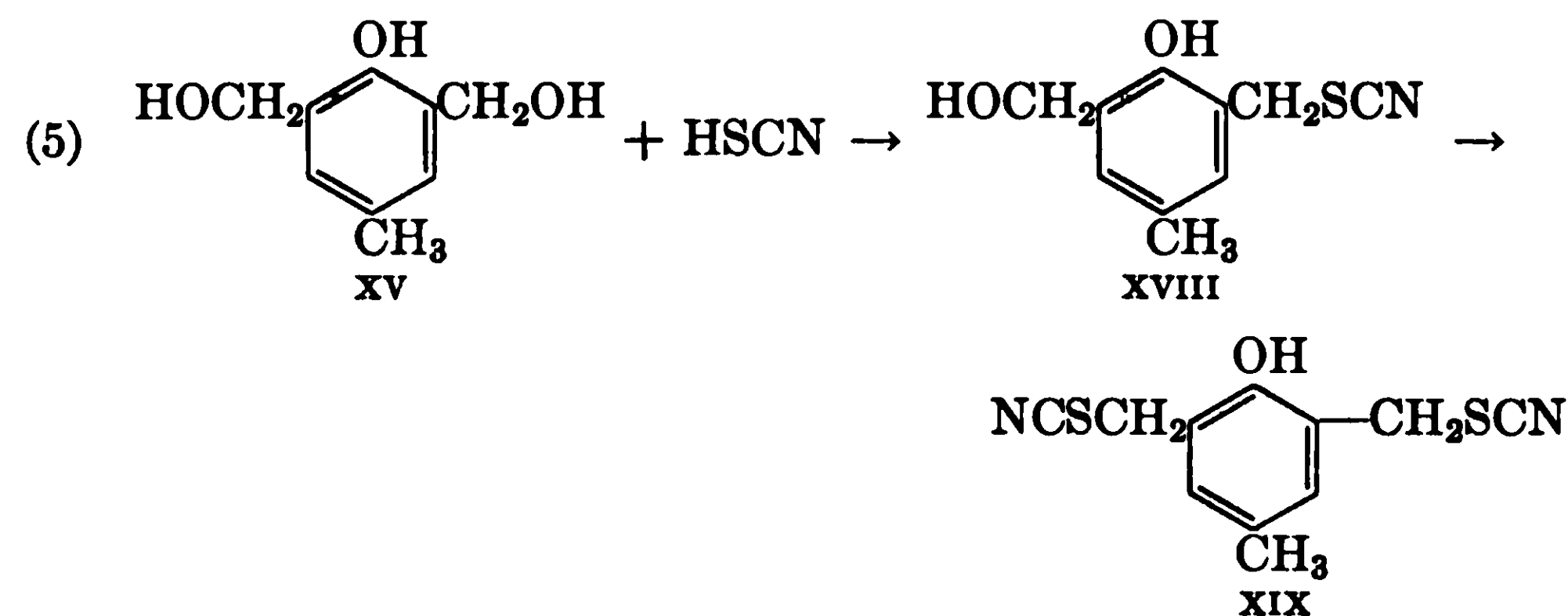
Nitrous acid reacts with phenol alcohols in a manner similar to nitric acid. Both acids replace methylol groups and give formaldehyde and nitro derivatives. Compounds XV, XVI, and XVII give 2,6-dinitro-*p*-cresol when reacted with nitrous acid. Compound XVI



results from treatment of either XV or XVII with nitrous acid under the proper conditions.⁸¹

Sodium nitrite in an acidic medium also has been used to nitrate dihydroxydiphenylkanes.^{28, 81}

Thiocyanic Acid. Thiocyanic acid reacts with phenol alcohols to give thiocyanomethyl derivatives,⁶⁸ equation 5. This reaction is



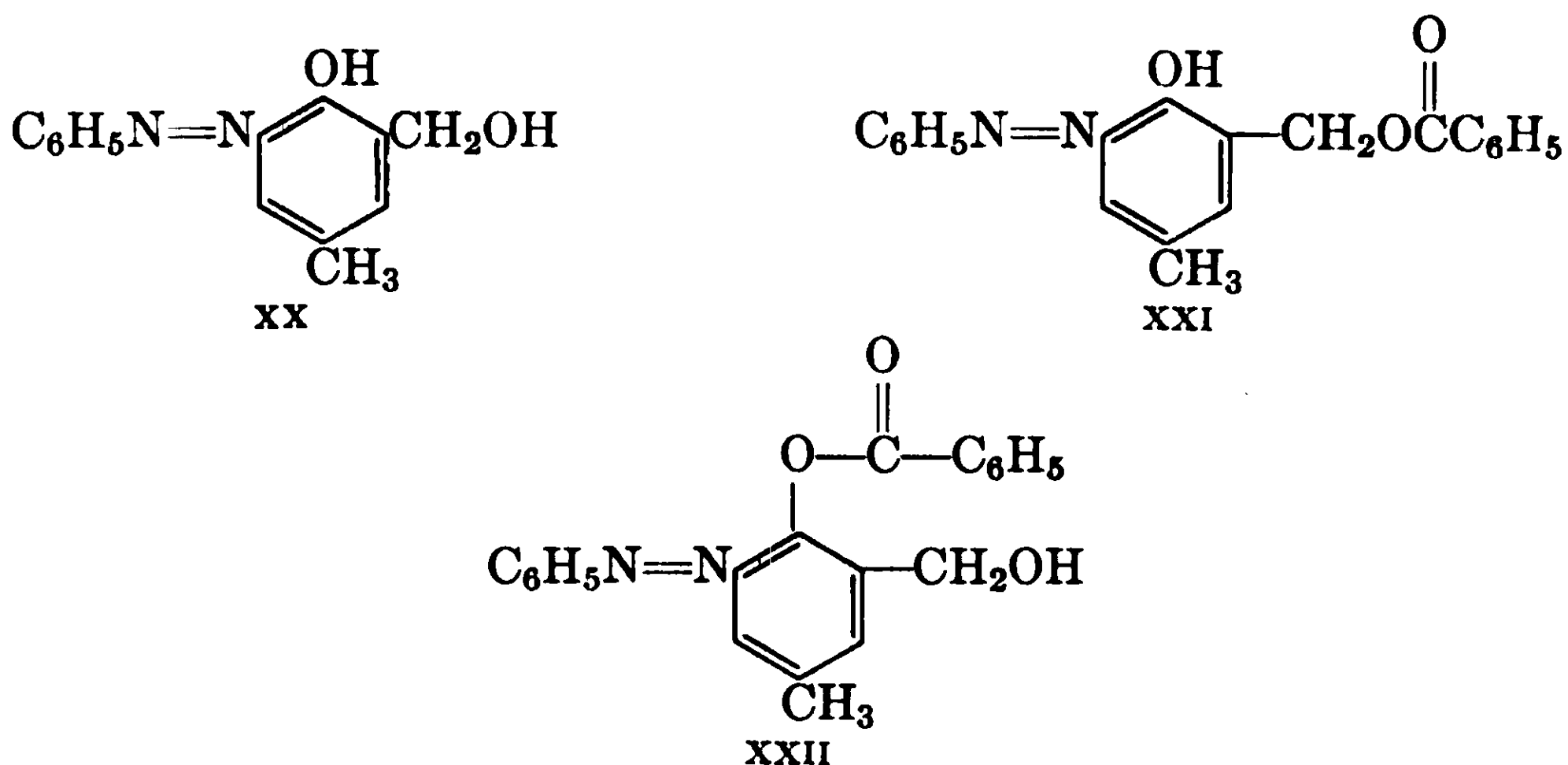
analogous to the reaction that occurs with halogen acids. Either XVIII or XIX may be obtained as the major product by proper control of reaction conditions. The thiocyano group behaves much like the halogen of a halomethyl phenol in that it is easily replaced by other groups. It has been reported that on heating to high temperatures they will give quinone methides.

ORGANIC ACIDS

Organic acids are poor reagents for the esterification of the phenolic hydroxyl group of dihydroxydiphenylalkanes or phenolic resins. The reaction is usually slow but it proceeds at a practical rate when a means for removing water, such as azeotropic distillation, is provided. However, acid anhydrides or acid chlorides, particularly in the presence of organic or inorganic bases, are effective acylating agents for dihydroxydiphenylalkanes.

The esterification of the hydroxyl groups of phenol alcohols with organic acids is almost invariably accompanied by condensation of the phenol alcohol. This side reaction is particularly bothersome with the more reactive phenol alcohols. On the other hand, both the methylol and phenolic hydroxyl groups of a phenol alcohol are acetylated with acid anhydrides and acid chlorides with few side reactions. Numerous investigators have used the esters as derivatives for elucidating the structure of both resinous and non-resinous phenolic products.^{21, 82-87} The acetylation number has been found useful as a measure of the hydroxyl content of such products. Dihydroxydiphenylmethanes and dihydroxydibenzyl ethers may be separated as their acetate esters and recovered by hydrolysis of the esters. On the other hand, esters of phenol alcohols seldom yield phenol alcohols on hydrolysis.⁸⁶ The only exception found was the hydrolysis of the acetate esters of 2,4-dihalo-6-methylolphenols.^{88a} Surprisingly enough, the alcoholysis of the esters of phenol alcohols results in a high yield of alkoxymethylphenols.⁸⁸

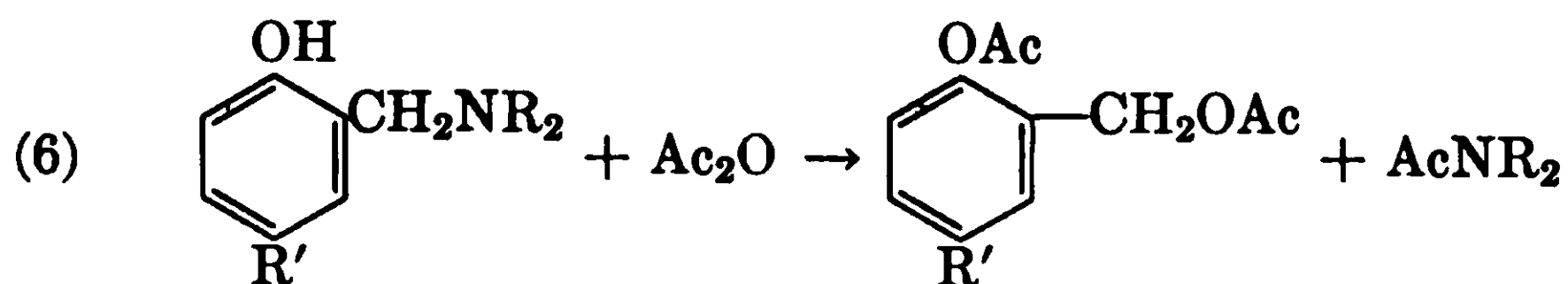
Zigeuner and Ziegler⁵⁶ have reported an interesting esterification reaction. When the sodium salt of XX was treated with benzoyl chloride, XXI rather than XXII was formed. The reaction was car-



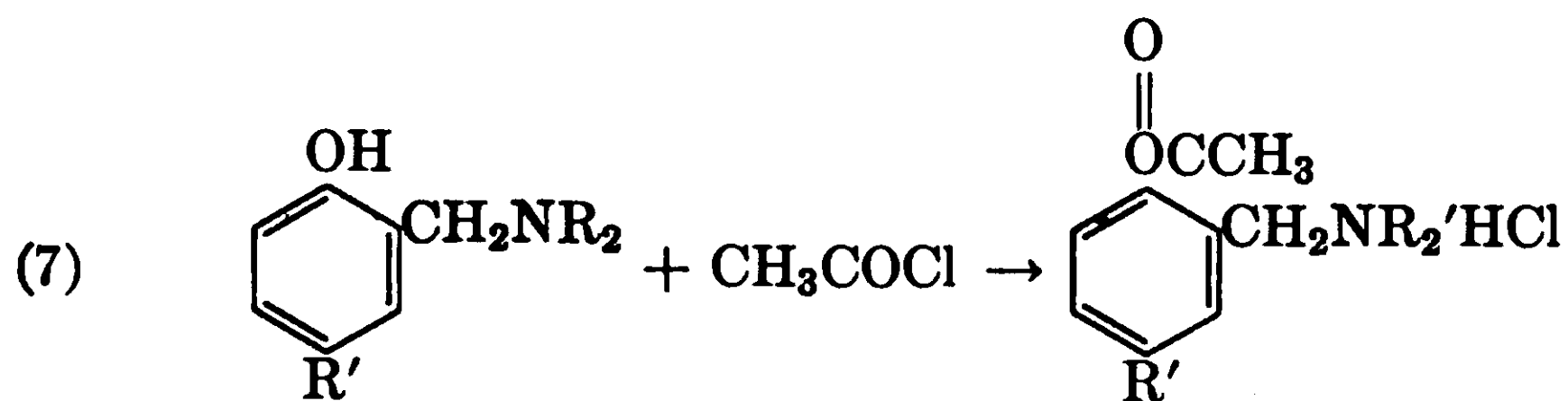
ried out in benzene solution. Compound XXI was also formed by the reaction of the corresponding chloromethylphenol with sodium benzoate in benzene solution. This is an elegant procedure for the preparation of esters of only the methylol groups on a phenol alcohol. Occasionally, the reaction may be effected by direct reaction of an organic acid or anhydride, rather than its salt, with the halomethylphenol.⁴⁰

An important group of esters is prepared by reaction of the phenolic hydroxyl group of phenol alcohols, dihydroxydiphenylalkanes, etc., with aromatic and occasionally aliphatic sulfonylchlorides.⁸¹ Reaction is usually effected by shaking or stirring the phenolic compound in a small molar excess of 1–5% aqueous caustic with the sulfonylchloride dissolved in a solvent such as benzene.^{80,89} The sulfonyl esters are frequently used where blocking of the phenolic hydroxyl group is an advantage.^{14,90} The toluenesulfonates of phenolic resins are claimed to be colorless and stable.⁹¹

Mannich bases derived from phenols yield, on treatment with acid anhydrides, the esters of the corresponding phenol alcohols,^{92,98} equation 6. If 1 mole of an acid chloride is substituted for the anhydride



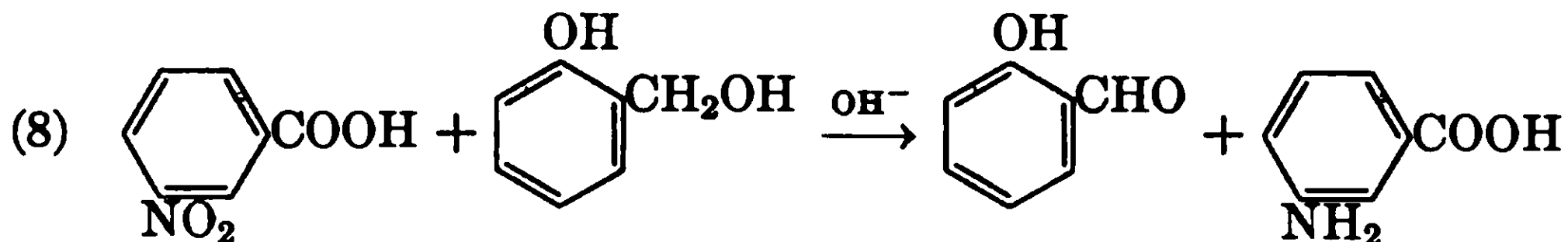
only the phenolic hydroxyl group is acetylated,⁹⁴ equation 7.



OXIDATION

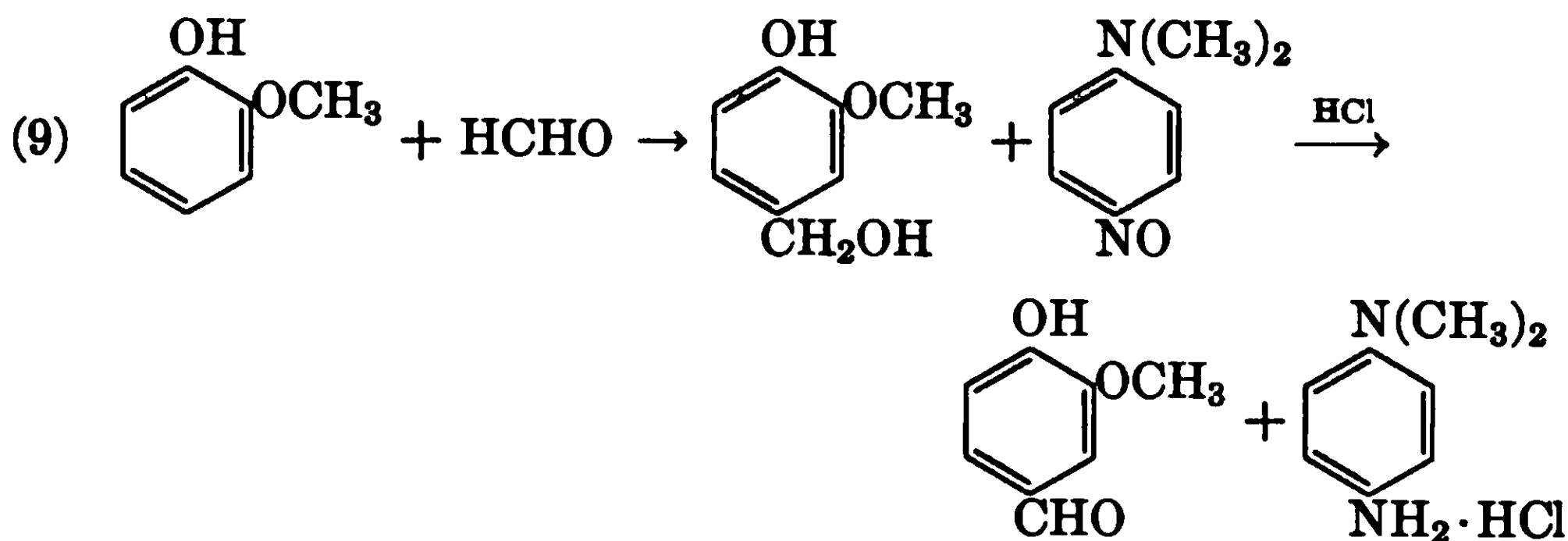
The oxidation of phenol-aldehyde condensation products, unless carefully controlled, may yield such complex products that their isolation and purification may present almost insurmountable difficulties. However, by the proper choice of conditions and reagents, oxidations sometimes may be effected in which pure compounds are obtained in reasonable yield.

Phenol alcohols react with *m*-nitrobenzoic acid or *m*-nitrobenzenesulfonic acids to form phenolic aldehydes,⁹⁶⁻¹⁰⁰ equation 8. The reac-

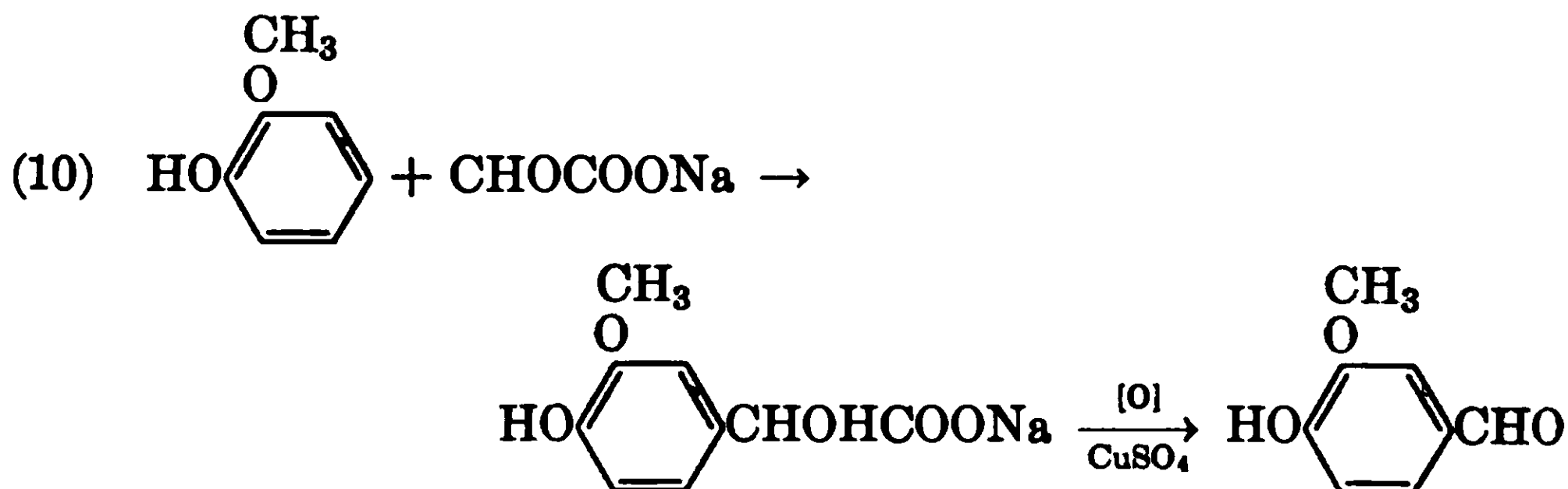


tion is carried out by refluxing the phenol alcohol with an alkaline solution of the aromatic nitro compound. The reaction has been useful in preparing derivatives suitable for the identification of phenol alcohols; it has also been used in the commercial synthesis of vanillin.

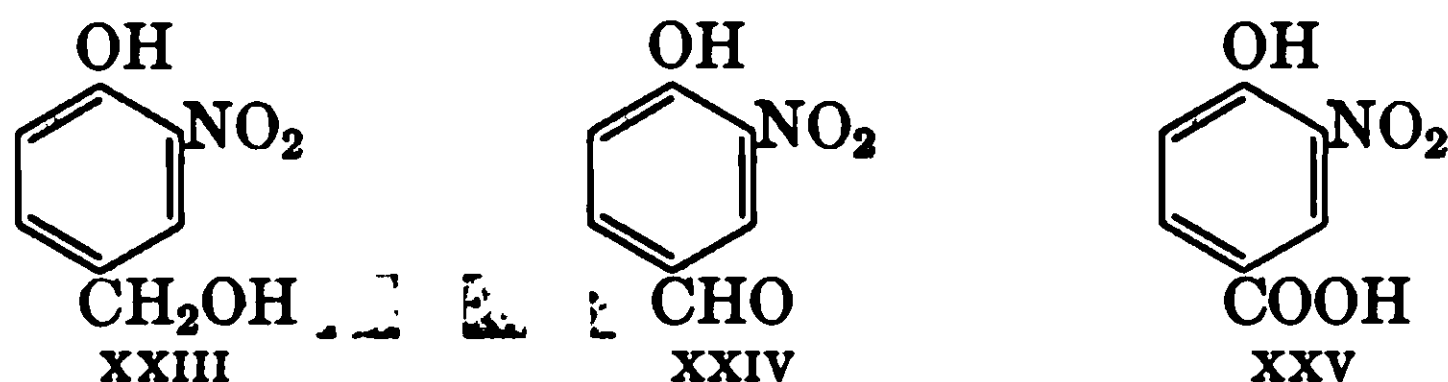
Nitrosobenzene or phenylhydroxylamine also have an oxidizing action on phenol alcohols when used in the presence of cupric oxide as catalyst.¹⁰¹ Vanillin may be prepared by the treatment of guaiacol with formaldehyde followed by oxidation of the methylol derivative with *p*-nitrosodimethylaniline in the presence of methanol and hydrogen chloride,¹⁰² equation 9.



The monoalkyl ethers of catechol condense with sodium glyoxalate to give substituted methylol derivatives. These compounds may be oxidized to the corresponding phenolic aldehyde in yields up to 80% of theory by refluxing with aqueous cupric sulfate or nitrobenzene,¹⁰³ equation 10.

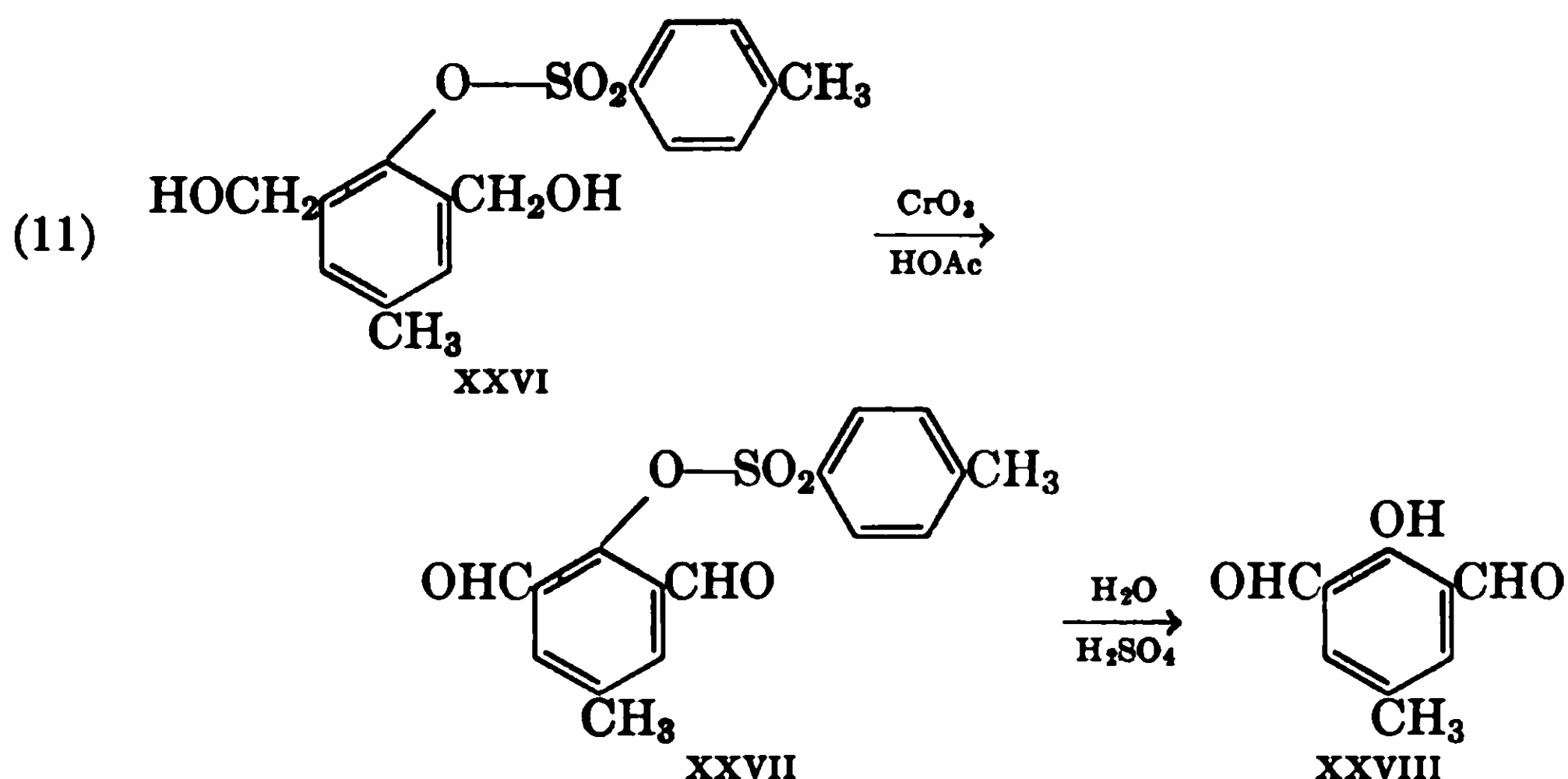


Certain phenol alcohols may be oxidized smoothly to phenol aldehydes with potassium permanganate if the amount of reagent and reaction conditions are carefully controlled. Fishman¹⁰⁴ found that 2-nitro-4-methylolphenol, XXIII, could be converted either to the aldehyde XXIV or acid XXV by proper regulation of the quantity of

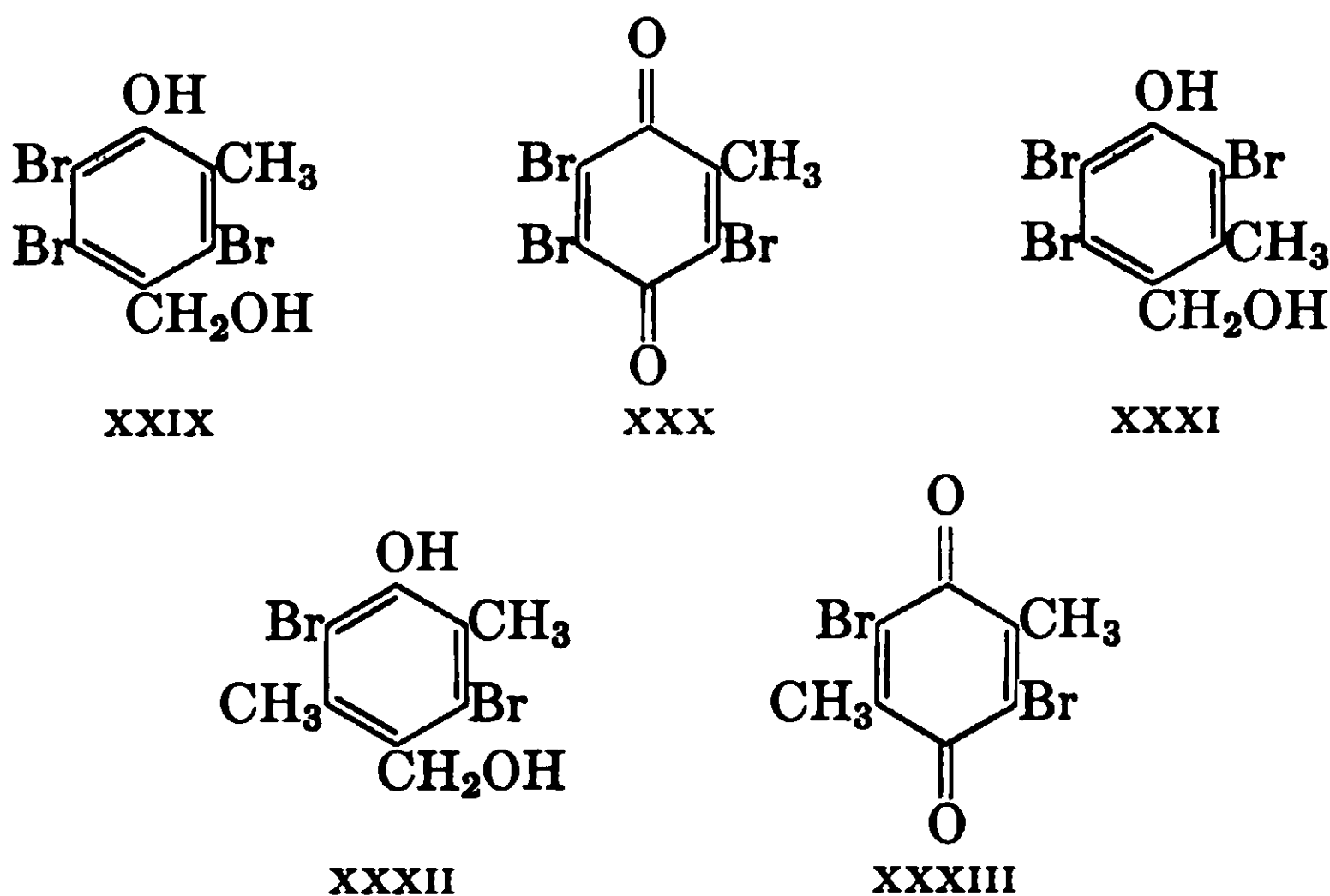


reagent. The *ortho*-methylol compound reacts in a similar manner.¹⁰⁵

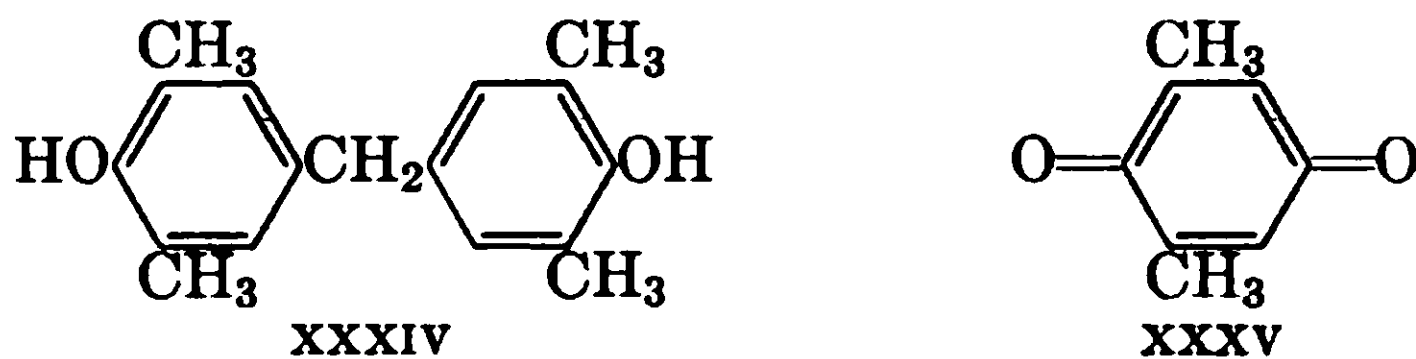
With phenol alcohols, susceptible to oxidative breakdown, blocking of the phenolic hydroxyl group by methylation before oxidation is often employed. After methylation of the phenolic hydroxyl group, the methylol groups are easily converted to carboxylic acid groups upon treatment with an alkali permanganate. The carboxyanisoles which result from such reactions have been quite useful as a tool in studying the structure of phenol alcohols.^{14, 80, 105-100} Blocking of the phenolic hydroxyl group of a phenol alcohol by reaction of the alcohol with *p*-toluenesulfonyl chloride has been used similarly. The ester has an advantage over the ether in synthetic work since it is more easily converted to the free phenol. Ullmann and Brittner⁸⁰ obtained a 98% yield of XXVII by treating XXVI with sodium dichromate in acetic acid. Compound XXVIII was obtained by the hydrolysis of XXVII, reaction 11.



Quinones may be formed by the mild oxidation of suitable phenol alcohols. For example, XXIX was oxidized to XXX with nitric

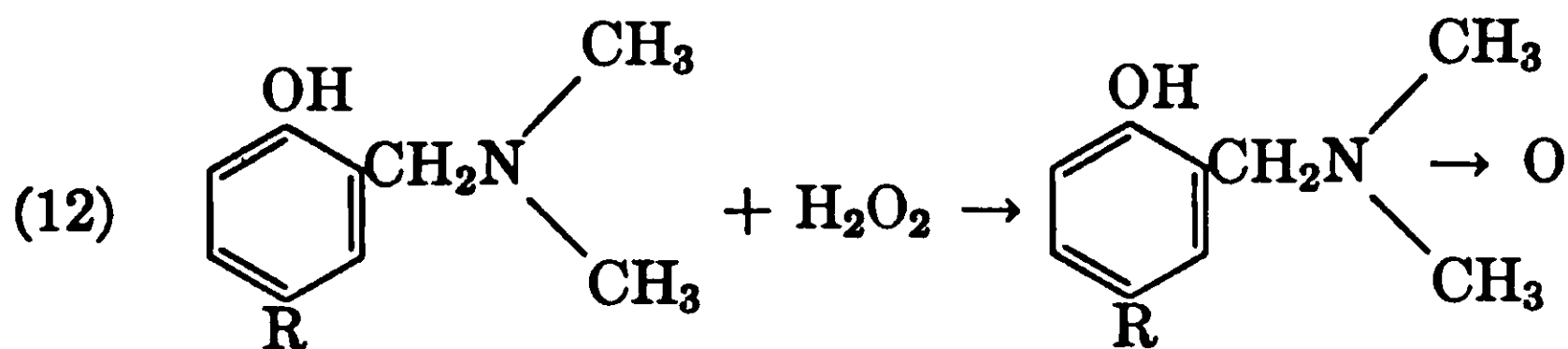


acid.⁴² The same quinone is also obtained by oxidation of XXXI.¹¹⁰ Chromic acid in glacial acetic acid as well as nitric acid will convert XXXII to XXXIII.⁵¹ Nakamura¹¹¹ obtained a dinuclear dimethylol-quinone on oxidation of saligenin with manganese dioxide. As expected, the methylol derivatives of hydroquinone are easily oxidized. Ferric chloride was found sufficient for conversion of dimethylol- and tetramethylolhydroquinone to the corresponding quinones.⁵⁴ With these compounds the oxidation of the phenolic hydroxyl groups was possible while the methylol groups were maintained intact. Tetra-(chloromethyl)hydroquinone was converted to the corresponding quinone by the use of chromic oxide. Quinones also may be obtained by oxidation of dihydroxydiphenylmethanes. Auwers,¹⁹ who was one of the first to study the reaction, found that XXXIV was converted to XXXV by treatment with chromic acid in glacial acetic acid.

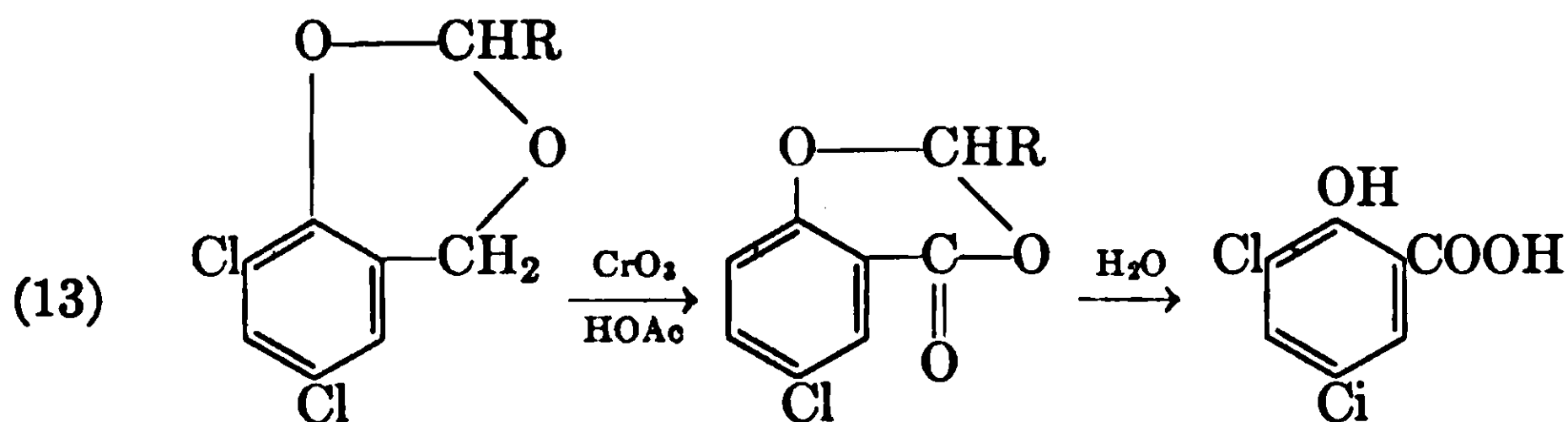


Steiner¹¹² obtained similar results with 4,4'-dihydroxy-2,2'-dimethyl-5,5'-diisopropylidiphenylethane. It appears likely that a dihydroxydiphenyl ketone is an intermediate in the oxidation of dihydroxydiphenylmethanes to quinones.¹¹³

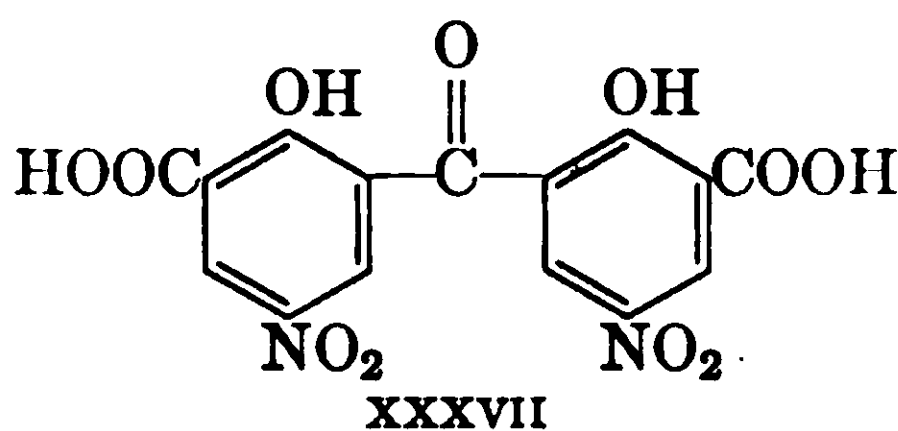
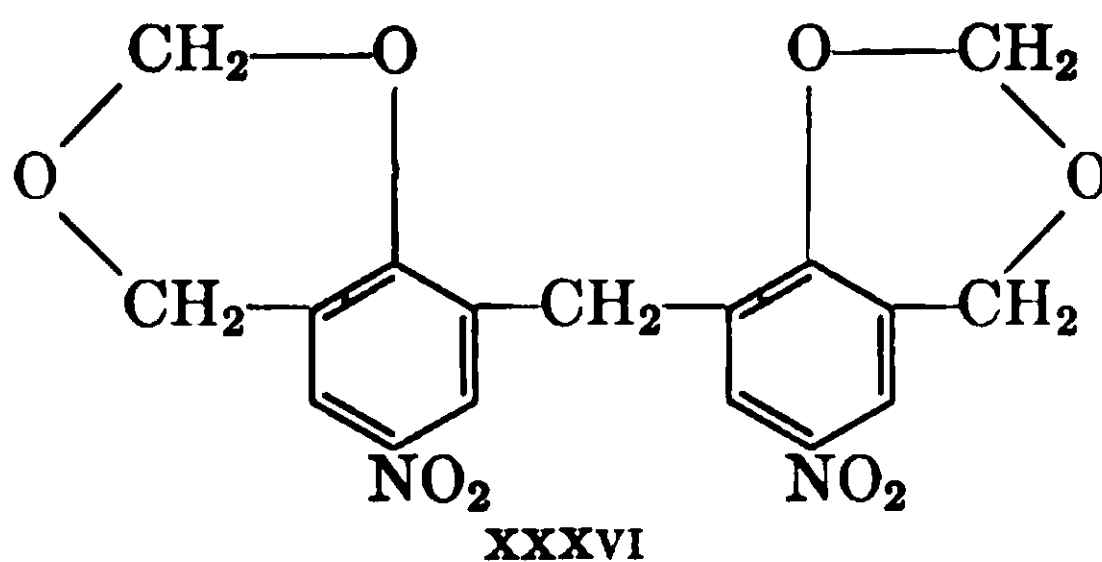
Of the less common phenolic products, the oxidation of the benzodioxans and the Mannich bases are of interest. The Mannich bases are oxidized to amine oxides by the action of hydrogen peroxide, equation 12. The products are water-soluble crystalline solids.¹¹⁴



The methylene bridge adjoining the benzene ring of a benzodioxan is oxidized to a carbonyl group, reaction 13. The carbonyl derivative



may then be hydrolyzed to a salicyclic acid derivative. Numerous substituted benzodioxans have been oxidized in this fashion.^{58, 115-119} With compound XXXVI, oxidation followed by hydrolysis gave the ketone, XXXVII, showing that both the methylene group adjoining the ring in the dioxan structure and the methylene bridge between the phenol rings may be oxidized without destroying the phenol.



It is of interest to note that Hall¹¹⁸ has found that novolac resins are spontaneously oxidized in the solid state on contact with air. Resins with an average molecular weight of 2890 were degraded in 163 hours by contact with oxygen at 70°C. to a product with a molecular weight of only 1165. The mechanism of breakdown was complex but was probably of peroxide and quinone origin. Infrared data re-

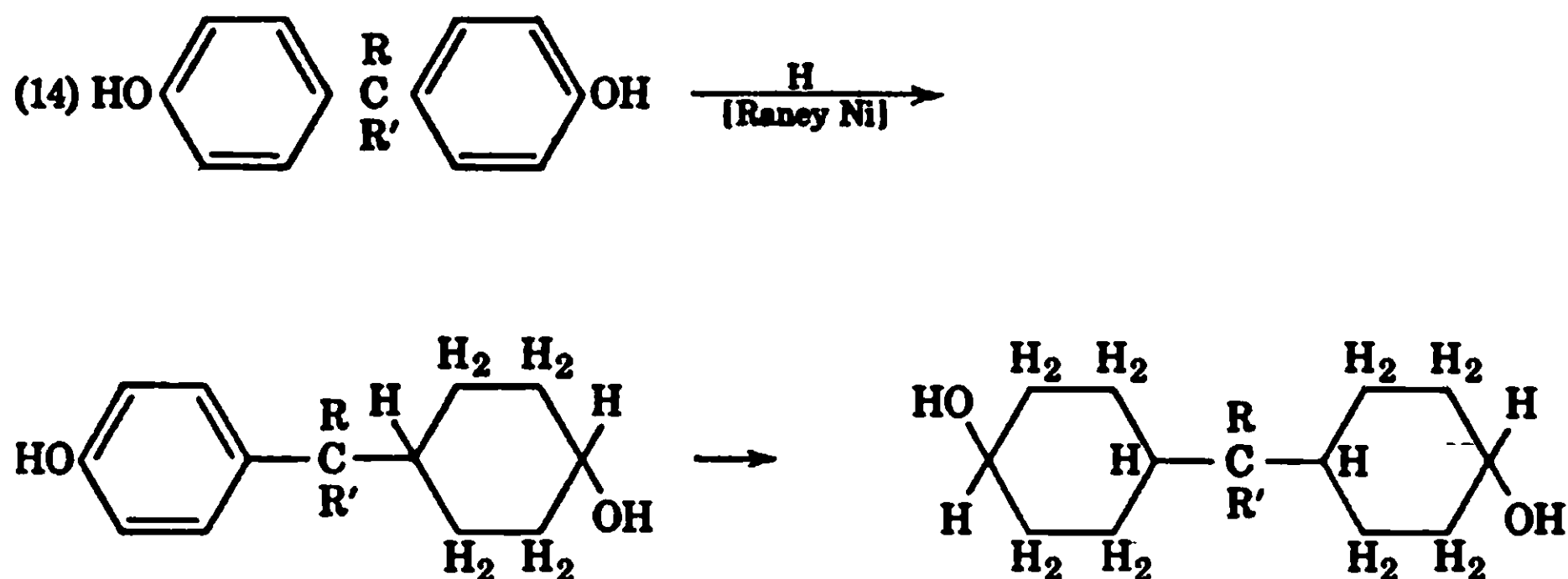
vealed the presence of benzophenone-type linkages, indicating the oxidation of methylene bridges. Nakamura^{111,120} has also studied the oxidation of phenolic resins. Oxidation of novolac resins in alkaline media resulted in the formation of triphenylmethane type dyes.

Oxidation of bis(2-hydroxy-1-naphthyl)methane with lead tetraacetate has been reported to give a cyclic quinol ether, presumably by formation of an intermediate quinone methide.¹²¹

REDUCTIONS

The reduction of phenol-aldehyde products may be effected catalytically with hydrogen as well as with the conventional organic and inorganic reducing agents. A rough classification of the reactions may be made according to whether the reaction occurs at the benzene ring or on the lateral groups attached to the ring. Reduction of the ring usually requires more severe conditions than reduction of the lateral substituents and leads to non-phenolic products.

Sheehan and Laubach,¹²² who studied the reduction of the rings of dihydroxydiphenylalkanes, were able to obtain reduction of either one or both of the benzene rings by controlling reaction conditions, equation 14. Raney nickel was the catalyst.



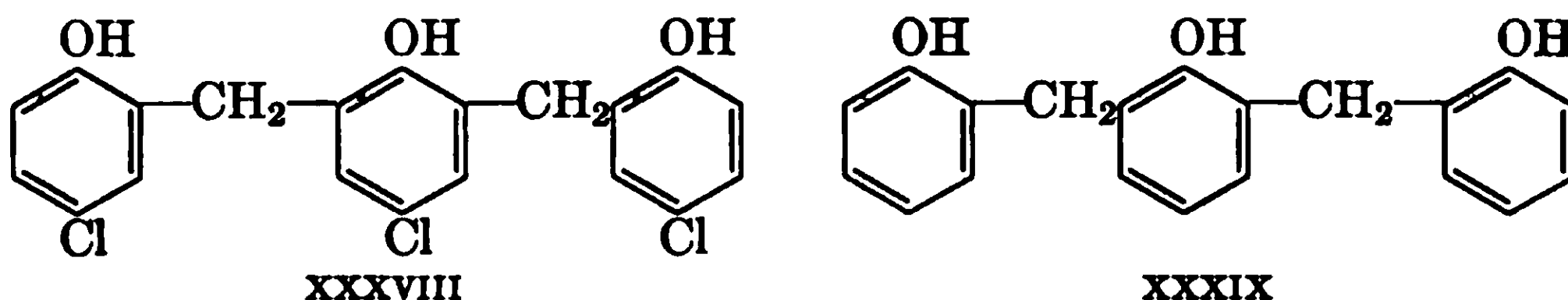
The reduction of the ring of a phenol alcohol presents certain problems on account of the strong tendency of the phenol alcohol to condense at the temperatures necessary for reduction. It has been reported, however, that with ruthenium oxide as catalyst *p*-cresol dialcohol has been reduced to 2,6-dimethylol-4-methylcyclohexanol, 2,4,6-trimethylcyclohexanol, and 2-methylol-4,6-dimethylcyclohexanol.¹²³

In considering the reduction of phenol-aldehyde products where reduction occurs on atoms or groups attached to the phenol ring similar reactions will be grouped together, regardless of whether the parent

compound is a dihydroxydiphenylalkane, phenol alcohol, or some other type of phenolic product.

The methylene bridge of a dihydroxydiphenylalkane or a phenolic resin may be severed by reduction. Boehm¹²⁴ and also Fries and Hübner¹²⁵ have reported that the methylene derivatives of various phenols may be reduced to the starting phenol or to a methyl derivative thereof. Novolac resins have been decomposed under reducing conditions.^{126, 127} Waterman and Veldman, who used molybdenum as catalyst, recovered phenol, benzene, cresol, and toluene as the principal products of reductive decomposition.¹²⁷

The removal of ring halogen atoms from phenol-aldehyde products is of considerable importance for synthetic purposes. A halogen may often be used to block a reactive ring position while a reaction is being carried on and then subsequently removed. Sodium metal and an alcohol have found widespread use for this purpose and are effective in removing halogens from dihydroxydiphenylmethanes,¹²⁸⁻¹³⁰ phenol alcohols,^{51, 131} and Mannich bases derived from phenols.¹³² An example of the use of halogens as a blocking agent is found in work of Finn, Lewis, and Megson.¹²⁹ The hitherto unknown trinuclear compound XXXIX was prepared from the corresponding derivative of *p*-chlorophenol XXXVIII by treatment with sodium in amyl alcohol. The chlorinated compound is easily prepared by the reaction of *p*-chlorophenol dialcohol with excess *p*-chlorophenol.

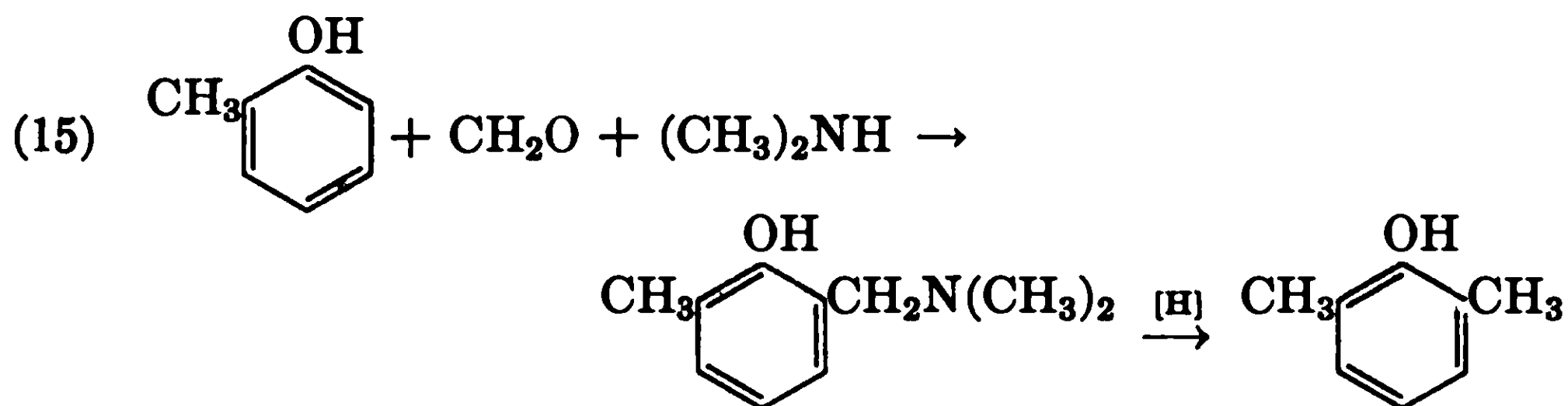


In addition to metallic sodium in alcohol, halogens may be removed from phenolic products with hydrogen in the presence of a palladium catalyst deposited on charcoal^{130, 131} or in the presence of Raney nickel or Raney nickel-aluminum alloy.¹³³ Sodium in liquid ammonia also is effective.¹³⁴

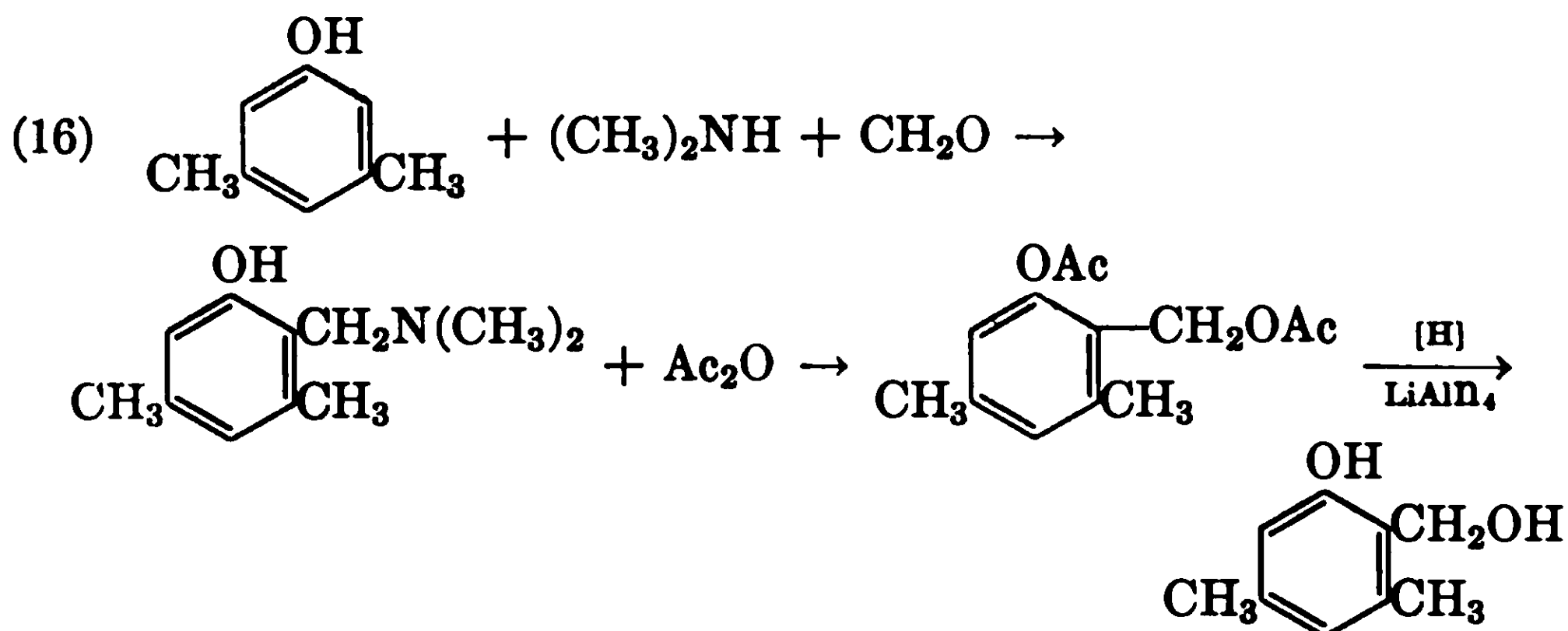
An important means for the preparation of methyl-substituted phenols is the reduction of easily prepared substituted methyl derivatives of phenols, e.g., hydroxymethyl, halomethyl, acyloxymethyl, or dialkylaminomethylphenols. Copper chromite has been used widely as a catalyst for reductions of this type, particularly where phenol alcohols¹³⁵ or dialkylaminomethylphenols have been involved.¹³⁶⁻¹³⁹ Palladium-carbon,¹³⁹ Raney nickel,^{139, 140} and even sodium methoxide in methanol^{141, 142} are effective with the dialkylaminomethylphenols.

Zinc dust and hydrochloric acid have been used with the chloromethylphenols.¹³¹

An example of the reduction of a substituted methylphenol to obtain a particular methylphenol is found in the work of Carlin and Landerl.¹⁴⁰ These authors made use of the fact that the dimethylaminomethyl group enters the ring of *o*-cresol in the other *ortho* position. The Mannich base so obtained was then reduced to 2,6-dimethylphenol, a phenol difficult to synthesize by other means, reaction 15.



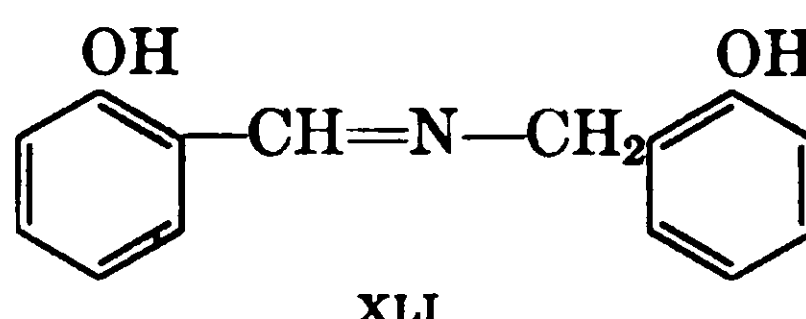
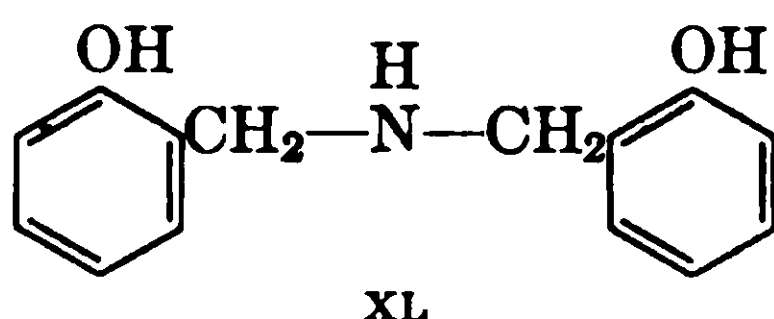
It is possible to prepare phenol alcohols by reduction of a phenol with an appropriately substituted methyl group. Finn and Musty^{143, 144} prepared the hitherto unknown 2-methylol-3,5-dimethylphenol from 3,5-xyleneol by the reaction shown in equation 16. At first inspection it would appear that hydrolysis of the acetate ester should give the desired phenol alcohol. However, hydrolysis of hydroxymethyl esters usually gives only resins, hence the necessity for the hydrogenation reaction. The reduction was carried out with lithium aluminum hydride.



Phenol alcohols have also been obtained by reduction of carboxylic acid derivatives of phenols with lithium aluminum hydride.^{131, 145} Freeman has found that better yields of the phenol alcohol are obtained if the phenolic hydroxyl group is acetylated before the reduction.¹⁴⁶

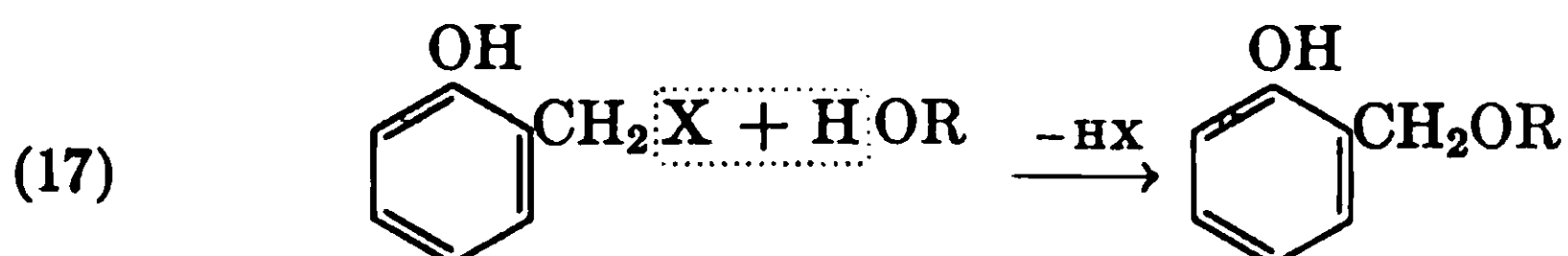
Duff and Furness¹⁴⁷ discovered that bis(hydroxybenzyl)amines such as XL may be prepared by heating phenols with hexamethylenetetra-

mine and boric acid in 2-ethoxyethanol. Hexamethylenetetramine in acetic acid has a specific dehydrogenating action on such compounds, and high yields of the corresponding Schiff's bases, XLI, are obtained. Schiff's bases, as well as the parent secondary amines, from eleven phenols were described.

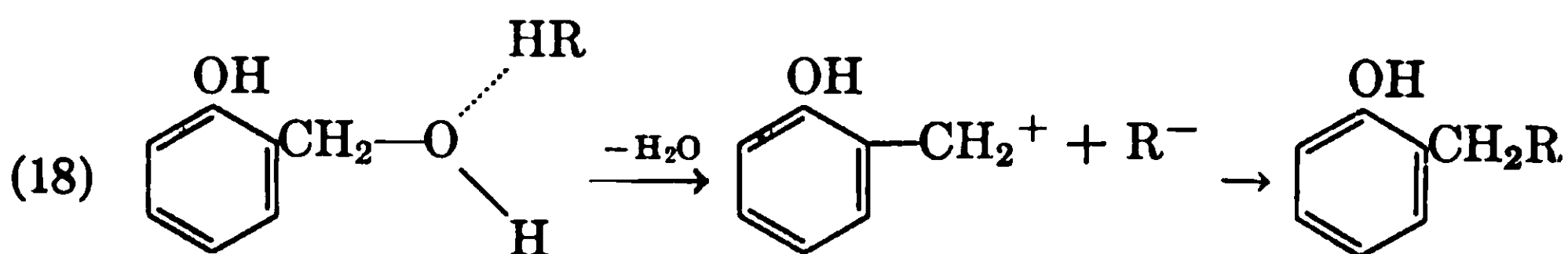


ALCOHOLS

The reaction of alcohols with certain phenolic products was investigated very early by Auwers and coworkers,^{41,51,57} who found that both phenol alcohols and halomethylphenols react with alcohols to form alkoxymethylphenols. (See also refs. 43, 65, 148.) The reaction is shown in equation 17, where X may be either a halogen or an hy-



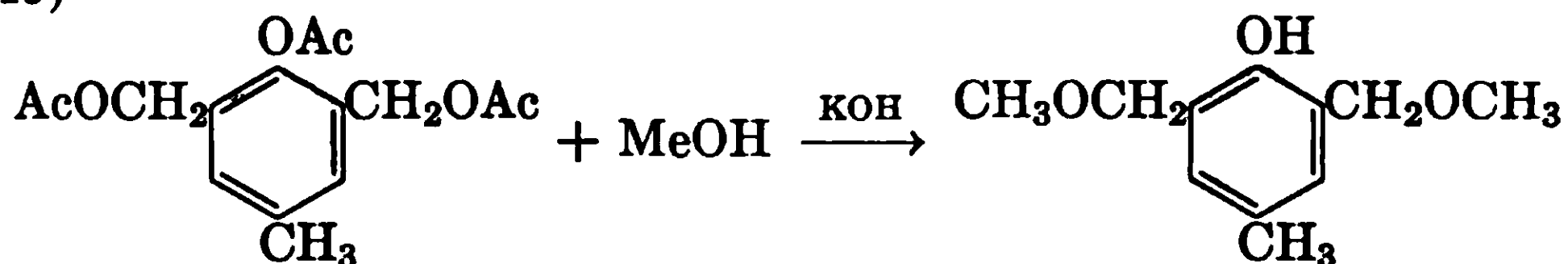
droxyl group. A phenol alcohol may also function as the alcohol, in which case a dihydroxydibenzyl ether is formed. (See Chapter 5.) That reaction occurs with heat alone; with other, less active alcohols a trace of acid catalyst is usually required. Ziegler³⁷ thinks that a halomethylphenol is the active intermediate in the cure of One-Stage resins where a halogen acid is used as a catalyst. In support of this theory, he and his coworkers have succeeded in reacting halomethylphenols with phenol alcohols to give dihydroxydibenzyl ethers and with phenols to give dihydroxydiphenylmethanes. 4-Methoxymethyl or 4-ethoxymethyldurenol was obtained by reaction of durenol with HCHO in methyl or ethyl alcohol.¹⁴⁹ The reaction was conducted at room temperature in the presence of sodium hydroxide or calcium hydroxide. The use of alkali is rather surprising. Hultsch^{150,151} pictures the reaction of a phenol alcohol with an alcohol as shown in equation 18.



The alkoxylation of One-Stage resins, particularly from trifunctional phenols, was introduced by Greth¹⁸² as a means for improving the hydrocarbon and oil solubility of such resins. The process has since achieved commercial importance in making heat-curable phenolic varnishes which are compatible with a variety of oils and resins. In practice, alcohols with 3 to 5 carbon atoms are commonly used, and only part of the methylol groups are reacted, depending on the oil compatibility required. The products obtained still possess curing properties, although the rate of cure is reduced. Cure results both through reaction of free methylol groups remaining in the resin and by partial splitting off of the alkoxy groups. The alcoholysis of urea and melamine resins to obtain oil solubility is also widely practiced.

An elegant procedure for the preparation of alkoxymethylphenols is the treatment of an acylated phenol alcohol with an alcohol in the presence of caustic. Barthel⁸⁸ obtained a 90% yield of di(methoxymethyl)-*p*-cresol by treating 2,6-bis(acetoxymethyl)-4-methylphenyl acetate with methanol and KOH, equation 19. Alkoxymethylphenols

(19)



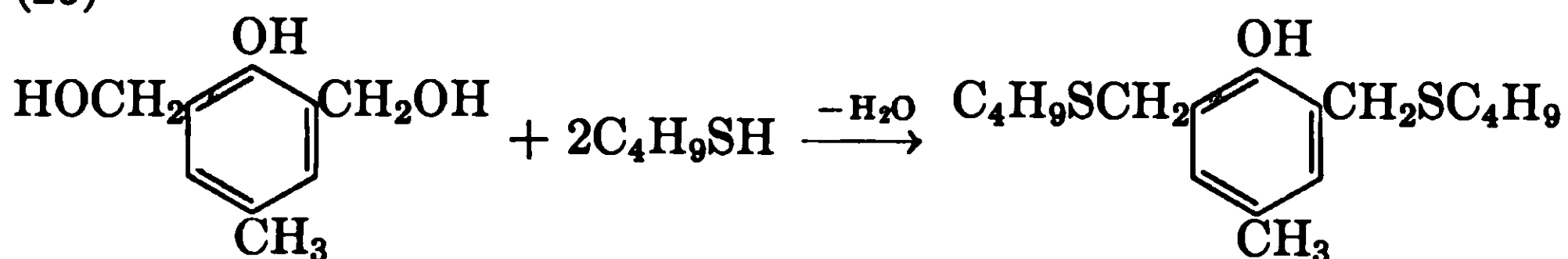
can be substituted for the alkoxymethylphenyl esters in the reaction with similar results.⁶⁶

Krumbhaar¹⁸⁸ has reported a very interesting procedure for preparing ethers with polyhydric alcohols. Phenol alcohols such as *p*-*tert*-butyl or amylphenol dialcohol react with ethylene glycol or glycerine in the absence of catalysts by the simple application of a vacuum. As a rule a pressure of 10 mm. or lower is necessary at 15°C., 15 mm. at 20°C., or 20 mm. at 25°C. Under such conditions it is claimed that reaction starts immediately and proceeds rapidly with the evolution of water. The maximum amount of glycerine or glycol that combines with the phenol alcohol is 1 mole per mole of the phenol dialcohol. If the dialcohol is recrystallized before use, the final ether is obtained as white crystalline clusters. The structure of the product was not given, but reaction presumably occurs with the elimination of water from a methylol group and a hydroxyl group of the polyol.

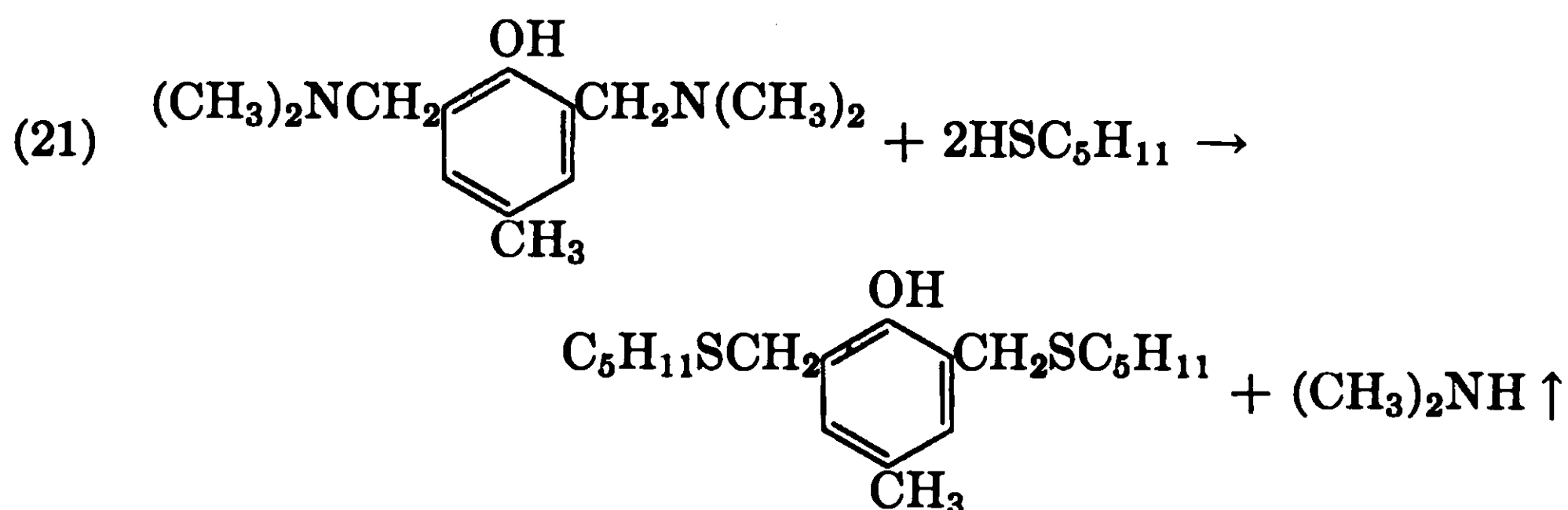
Thiols also condense with the methylol groups of phenol alcohols. Ruderman and Fettes¹⁸⁴ condensed 1-butanethiol with *p*-cresol dialcohol using either anhydrous BF_3 or HCl as catalyst. The product, a crystalline solid, contained two atoms of sulfur, showing that the

hydroxyl group of the methylol group was eliminated during reaction, equation 20. Similar products can be formed by refluxing phenolic-

(20)



type Mannich bases with mercaptans,¹⁵⁵ equation 21.

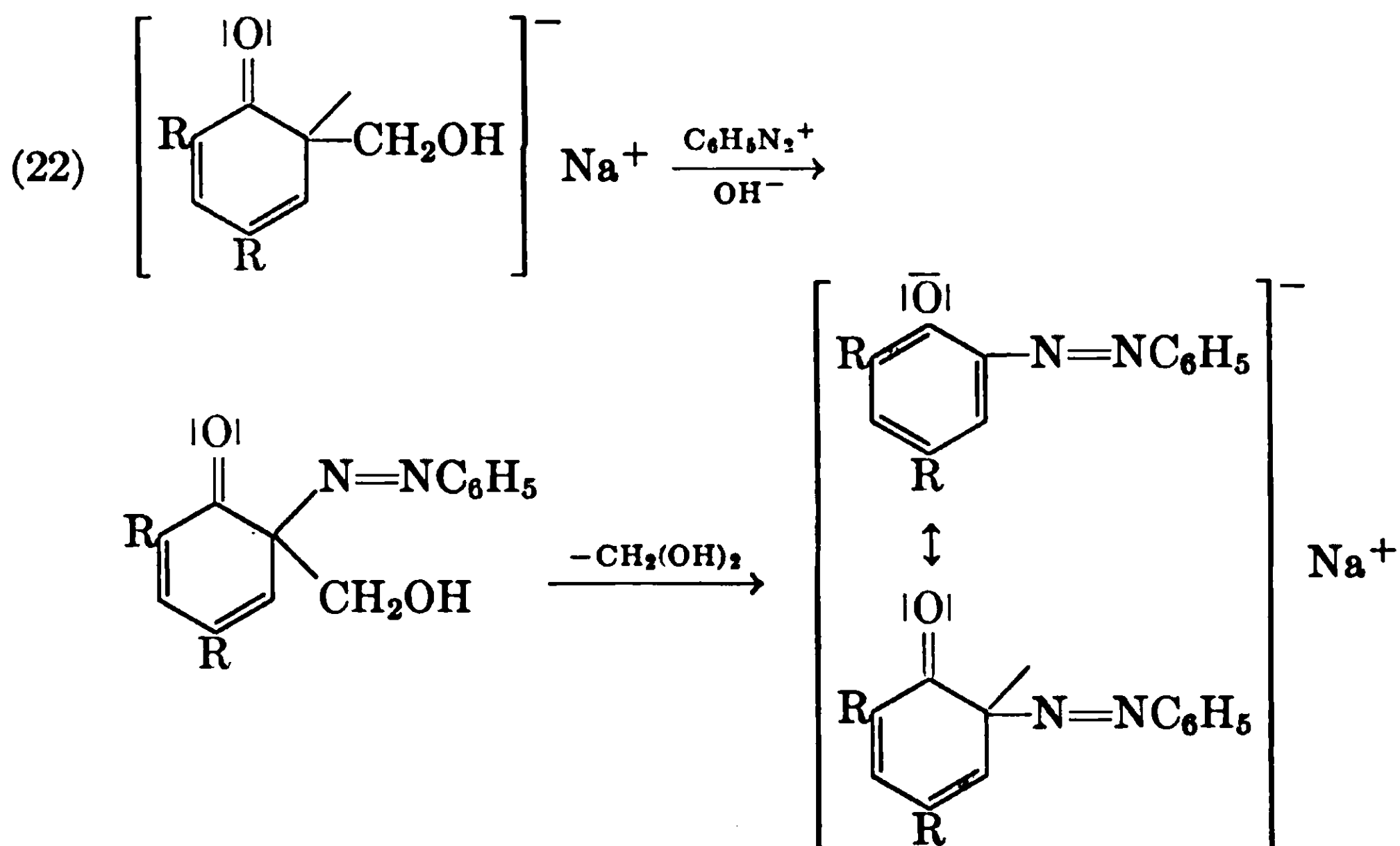


DIAZONIUM COMPOUNDS AND QUINONE IMINES

The action of diazonium compounds on phenolic products is of interest to the phenolic resin chemist mainly as a tool for elucidating structure and reaction mechanism. The reactions fall into three categories: (a) those in which coupling occurs at a free *ortho* or *para* ring position; (b) those in which displacement of a methylol group or derivative of a methylol group occurs; and (c) those in which cleavage at a methylene or alkylidene bridge occurs. Only the last two types of reaction will be considered here.

Neber and Kubitzky¹⁵⁶ and Zipples¹⁵⁷ found that *ortho* and *para* methylol groups may be smoothly expelled as free formaldehyde from certain phenol alcohols by treatment with diazonium compounds at room temperature. This reaction has been thoroughly investigated.^{87, 88, 96, 168-184} The course of the reaction depends on the structure of the phenol alcohol. A general order of reactivity at the *ortho* and *para* positions has been found. (See page 91.)

The reaction is usually carried out in aqueous alkali, but glacial acetic acid also has been used as a reaction medium. Because the rate approaches that of an ionic reaction and is frequently quantitative, an ionic type of mechanism has been proposed by Ziegler and Zigeuner,⁸⁷ equation 22.



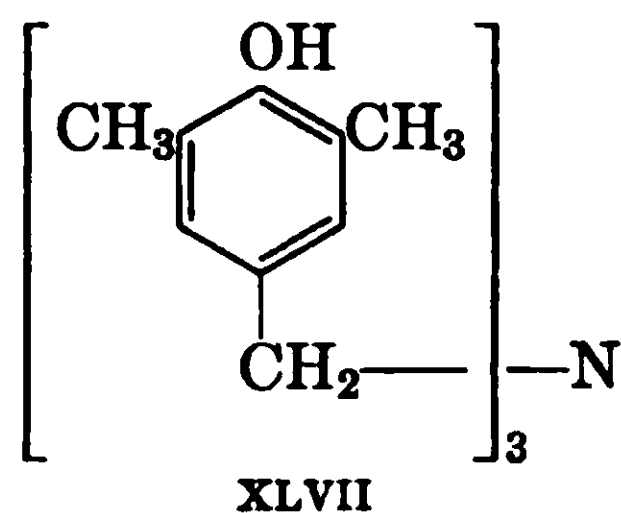
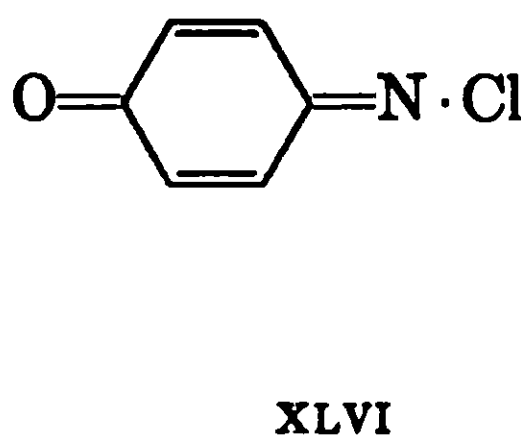
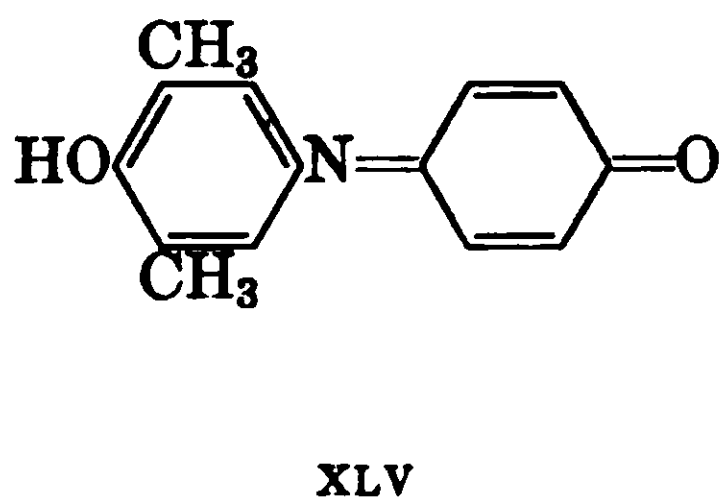
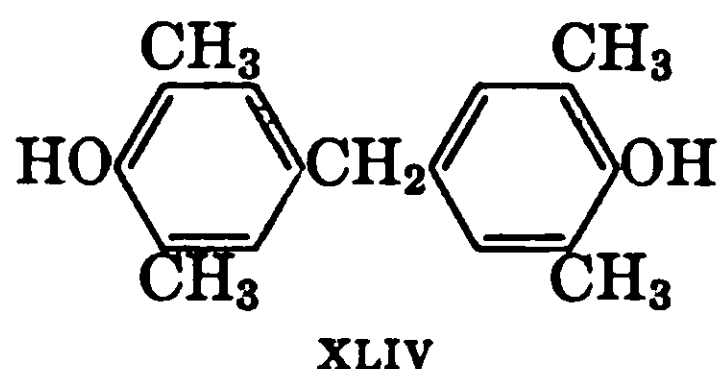
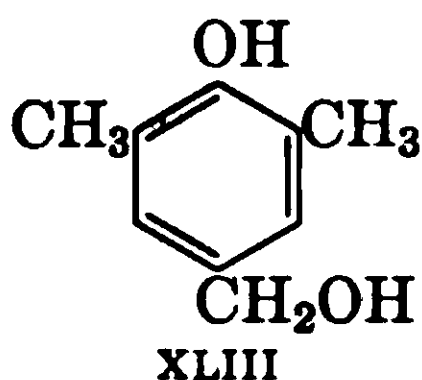
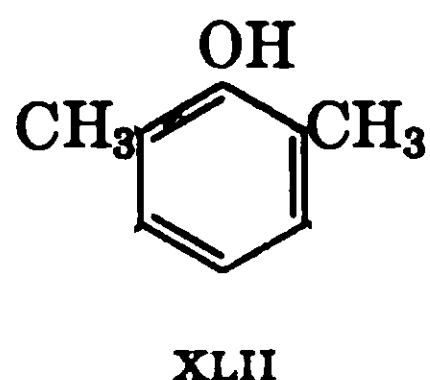
Substituted methylol groups can also be displaced by the action of diazonium compounds. On treating *p*-hydroxybenzhydrol, where one of the hydrogens attached to the carbon of the methylol group has been replaced by a phenyl group, with a diazo compound, Zigeuner and Ziegler¹⁶⁶ obtained *p*-hydroxyazobenzene and benzaldehyde. Certain functional derivatives of phenol alcohols appear to behave similarly to the parent phenol alcohol, although the data on such compounds are limited.¹⁶⁴ According to Zipples,¹⁶⁷ dihydroxydibenzyl ethers couple with diazonium compounds with the elimination of formaldehyde.

Although reaction may be somewhat slower than with the corresponding phenol alcohol, methylene and alkylidene bridges are split by the action of diazonium compounds. An aldehyde or ketone is formed as a by-product. The reaction has been studied by Brass and Sommer,¹⁶⁶ Mohlau and Strohbach,¹⁶⁶ Kubitzky,¹⁵⁶ Zipples,¹⁶⁷ and more recently by Zigeuner and Ziegler^{162, 164} and Marder and Ruderman.¹⁶⁷ As would be expected from the results with the phenol alcohols, the *p,p'*-dihydroxydiphenylmethanes are cleaved most readily. Compounds possessing *ortho,ortho*-methylene bridges are cleaved only with the highly active diazo compounds, such as *p*-nitrobenzenediazonium chloride.¹⁶² The splitting of alkylidene compounds apparently occurs by a mechanism similar to that suggested for the reaction with phenol alcohols. Compounds such as 4,4'-dihydroxydiphenylsulfide also are split by the action of diazo compounds.¹⁶⁶

Freeman¹⁶⁹ has developed an elegant procedure for the analysis of phenol alcohols in a phenol-formaldehyde reaction mixture. The

phenol alcohols are separated by means of paper chromatography, and nitrobenzenediazonium fluoroborate is used as an indicator. Quantitative results are obtained by weighing the spots developed after cutting out the spot with scissors.

The reaction of quinonimine chlorides, or quinone chloroimides as they are sometimes called, with phenolic compounds has not been studied as extensively as the diazo compounds discussed above. However, they appear to react with phenol alcohols and dihydroxydiphenylalkanes in a manner similar to the diazo compounds. According to Ziegler and Gartler,¹⁷⁰ compounds XLII, XLIII, and XLIV gave the same indophenol, XLV, when treated with quinonimine chloride, XLVI, in 4 *N* caustic solution. With phenol alcohols and methylene derivatives of phenols, the reaction was accompanied by the elimination of formaldehyde. The tribenzyl amine XLVII also gave a quantitative yield of the indophenol when treated with quinonimine chloride in 0.5 *N* sulfuric acid.¹⁷¹



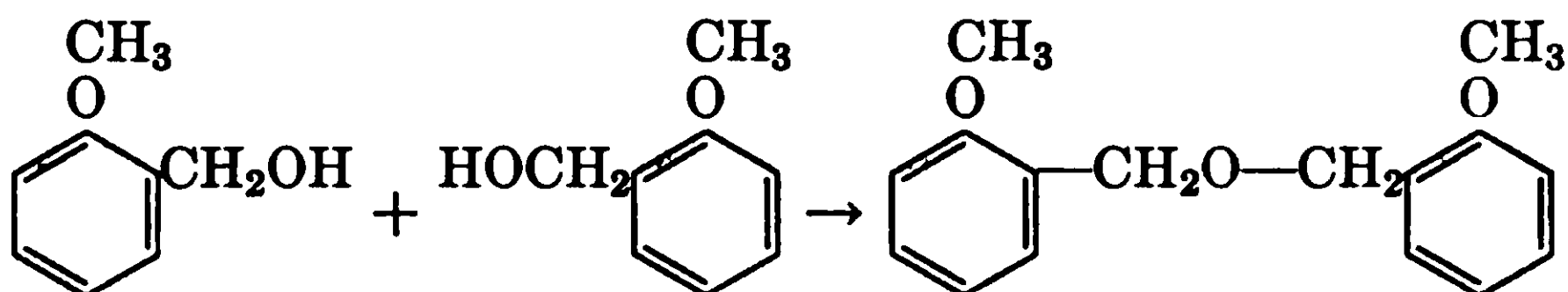
The fact that the reaction of diazonium compounds and quinonimine chlorides occurs with ease at room temperature, and exhibits strong preferential reactivity at certain positions on the phenol ring, makes them valuable in studying the structure of phenolic products. Frequently the location of a methylol group or a methylene bridge can be determined in a compound of unknown structure by simply coupling with one of the above reagents and observing the products of the coupling reaction.

REAGENTS FOR HYDROXYL GROUPS

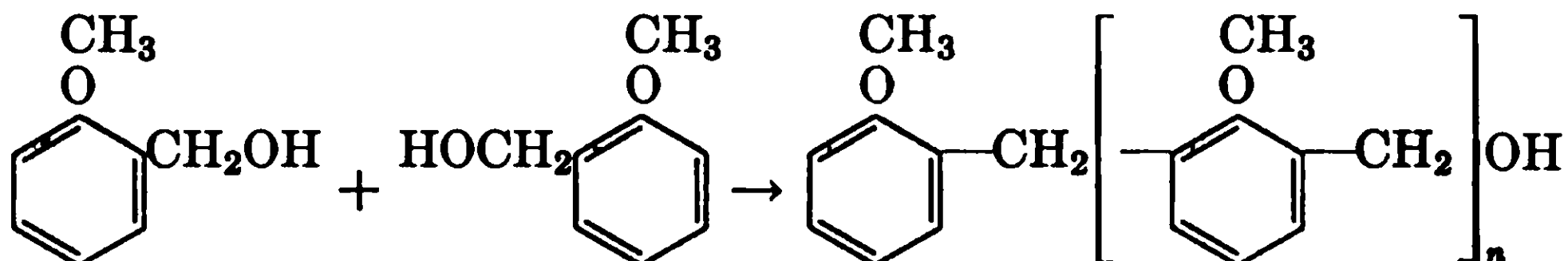
By subjecting phenol alcohols or dihydroxydiphenylalkanes to the action of alkyl halides or dialkyl sulfates alkylation of the phenolic

hydroxyl groups occurs.^{14, 21, 80, 105-107, 109} The reactions are usually conducted in the presence of an alkaline reagent and occur about as would be expected for the parent phenol. Ordinarily alkylation of the methylol groups does not occur. This permits the preparation of a great variety of alkylphenyl ethers having free methylol groups. The methylol groups in such compounds behave like the methylol groups of highly reactive benzyl alcohols. Besides undergoing the normal reactions of alcohols they are also capable of rapid self-condensation.^{172, 178} The self-condensation may result in formation of benzyl ethers, or methylene derivatives, reaction 23. There is evidence that the dibenzyl ether may be an intermediate in the second

(23a)



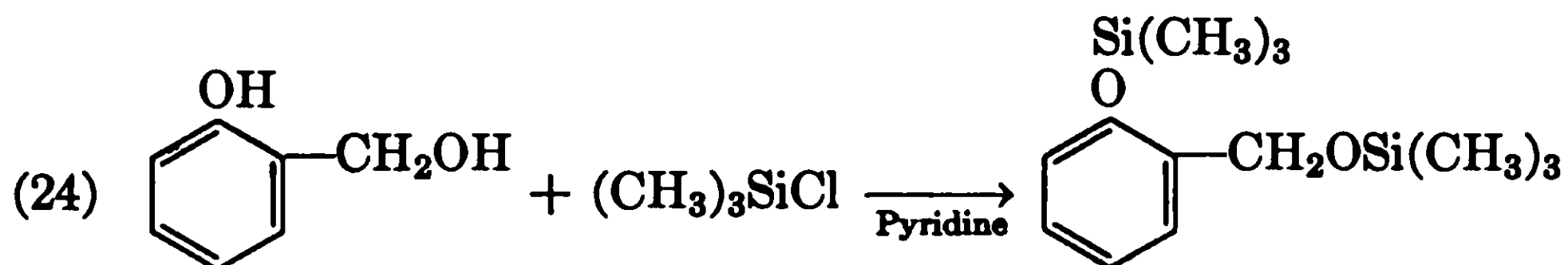
(23b)



reaction.¹⁷⁸⁻¹⁷⁵ Blocking of the phenolic hydroxyl groups of phenolic resins by ether formation improves color stability, alkali resistance, and oil solubility of phenolic resins.¹⁷⁹

Diazomethane can also be used to methylate the phenolic hydroxyl groups of phenol alcohols and dihydroxydiphenylalkanes. Gerber and Curtin¹⁷⁷ found that this reagent reacts only with the phenolic hydroxyl group of saligenin.

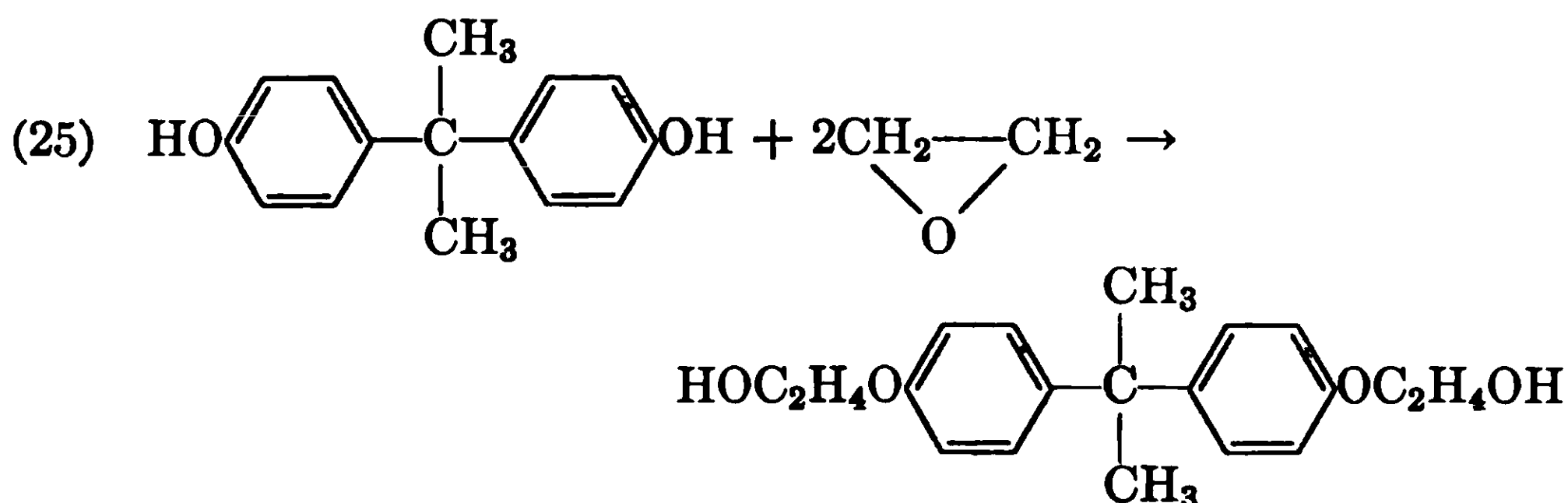
In contrast to diazomethane, trimethylchlorosilane reacts with the hydroxyl groups of both the phenolic hydroxyl and methylol groups of phenol alcohols, reaction 24. Martin¹⁷⁸ has prepared the trimethyl-



silyl derivatives of the phenol alcohols in a phenol-formaldehyde condensate. By fractional distillation of the derivatives, separation into

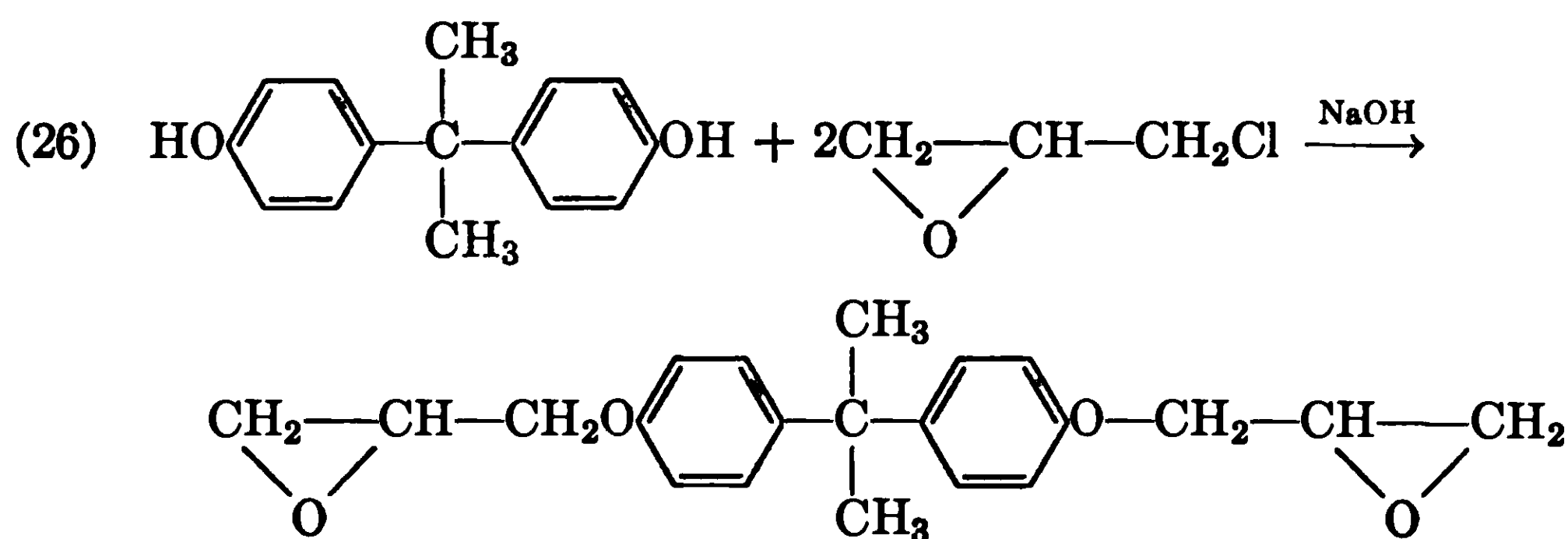
relatively pure components was possible. The compounds could then be hydrolyzed to the phenol alcohols under very mild conditions.

The reactions of alkylene oxides with phenolic products is not as selective as those with alkyl halides or dialkyl sulfates. With dihydroxydiphenylalkanes, glycolphenyl ethers are formed, reaction 25.

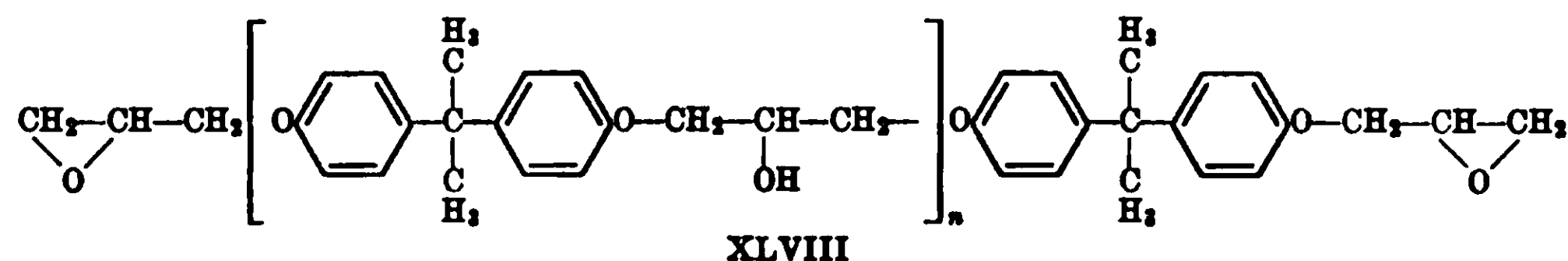


As the aliphatic hydroxyl groups are capable of further reaction with the alkylene oxide, polyglycol ethers also may result. This reaction even may occur to a minor extent with stoichiometric quantities of phenol and alkylene oxide, and it becomes the predominant reaction with an excess of the alkylene oxide. Both acids and alkalies are catalysts for the reaction, but alkalies are preferred. Glycol ethers of dihydroxydiphenylalkanes or low-molecular-weight novolac resins have been used as surface-active agents^{179,180} and as polyols.

When a dihydroxydiphenylalkane is condensed with an excess of epichlorohydrin in the presence of 2 moles of caustic a diepoxide is formed as the simplest product, reaction 26. Products of higher



molecular weight with terminal epoxide groups are formed as the combining ratio of the bisphenol to epichlorohydrin is increased.¹⁸¹⁻¹⁸⁴ These products may be represented by a general formula, XLVIII,



and have been referred to as polyepoxide resins or as ethoxyline resins as well as by several trade names. The resins have found use in surface coatings, adhesives, pottings, and casting and molding resins. They cure without the elimination of by-products on the addition of amines, acid anhydrides, or alkalis to products with excellent solvent and alkali resistance and good mechanical properties.

When phenol alcohols are treated with alkylene oxides, reaction may occur with both the phenolic hydroxyl groups and the methylol groups.¹⁸⁵ Reaction with the phenolic hydroxyl groups occurs much more rapidly than with methylol groups. This means that the phenolic hydroxyl groups react first and it permits the preparation of materials in which most of the phenolic hydroxyl groups have been reacted while many of the methylol groups remain free. According to Becker and Barthel,¹⁸⁶ such products are hardenable.

Brannon¹⁸⁷ has reacted phenolic-type Mannich bases with alkylene oxides. The products are quaternary ammonium compounds. They were recommended as catalysts for curing One-Stage phenolic casting and laminating resins.

ROTTLERONE CHANGE

The methylene derivatives of highly substituted polyhydroxyphenols in particular are susceptible to a disproportionation reaction which is sometimes referred to as the "rottlerone change."^{188, 189} The general reaction is shown in equation 27, where R and R' represent the hydroxyphenyl group attached to the methylene bridge.



Warm acidic or alkaline conditions promote the reaction, and it has been observed that the methylene derivatives derived from phloroglucinol or substituted phloroglucinols are more reactive than the methylene derivatives of resorcinol, for example. By the use of a reaction medium consisting of boiling acetic acid the formation of resinous by-products is minimized. However, some oils are usually formed. The oils are believed to be cyclic acetals. The reaction has been represented as a reversible hydrolysis reaction.

Carpenter and Hunter¹⁹⁰ have found that 2,4,6-tris(2-hydroxy-5-methylbenzyl)phenol on boiling with *p*-cresol and a trace of acid forms 2,4'-dihydroxy-5-methyldiphenylmethane. This example shows that the reaction may, in certain instances, be extended to the methylene derivatives of monohydroxyphenols.

PYROLYSIS

The pyrolysis of phenol-aldehyde condensation products has been explored as a means for synthesizing various phenol derivatives and for elucidating the structure of complex phenol-aldehyde reaction products. The studies relating to the use of pyrolysis for elucidating the structure of phenolic resins were covered in Chapter 4.

The pyrolysis of phenol alcohols has been used for the synthesis of methylphenols.^{191,192} For example, if *p*-cresol dialcohol is heated at 250°C. small yields of mesitol and 2,4-xyleneol are obtained. In the presence of alkalies the yield of the methylated products generally is higher than when alkali is absent. Best results are obtained with alkalies such as the oxides and hydroxides of alkaline earths and magnesium oxide and the borates of alkali metals. The pyrolysis of dihydroxydiphenylmethanes under similar conditions is reported to give methylphenols.

Niederl and coworkers¹⁹³ have condensed monohydroxyphenols with a variety of saturated aldehydes. Upon slow pyrolysis of the products the corresponding saturated alkylphenols were obtained. However, if methyl alkyl ketones are condensed with phenols and the bisphenols obtained are pyrolyzed, isoalkenylphenols, such as isopropenyl, isobutenyl, and isopentenyl phenol, may be formed.⁷¹ Jones¹⁹⁴ has described the preparation of butenylphenols by the slow pyrolysis of the condensation product of methyl ethyl ketone and phenol.

Vinylphenols have been obtained by heating the benzodioxans derived from the condensation of acetaldehyde or acetylene with various phenols.¹⁹⁵ The pyrolysis was conducted at 400–650°C. over Frankonite, and the yields of *o*-vinylphenols were essentially quantitative.

The catalytic cracking of unsymmetrical diarylethanes to styrenes has been reported.^{196,197} It is claimed the arylethane may carry hydroxy substituents, in which event a vinylphenol would be formed.

ION EXCHANGE

One of the more interesting reactions of phenol-aldehyde resins is their ability to function in ion-exchange reactions. As has been discussed elsewhere,¹⁹⁸⁻²⁰³ an ion-exchange resin is a solid material capable of exchanging ions held by functional groups in the resins with those of solutions with which it is contacted. The resin is in the form of an insoluble and infusible gel; otherwise it would swell excessively and

disintegrate when in contact with the solutions in which it is to perform.

The first ion-exchange materials were the zeolites and similar products. A variety of carbonaceous materials that had either been oxidized or sulfonated to produce products having functional groups capable of reacting with ions were also introduced at an early date. Coal, lignite, peat, etc., were the types of materials most often used in this capacity. In 1935 Adams and Holmes²⁰⁴⁻²⁰⁵ made the important discovery that certain synthetic resins also exhibited ion-exchange properties. The first synthetic resins to be used for this purpose were phenol-aldehyde condensation products derived from polyhydroxyphenols. The polyhydroxyphenols were reacted with sufficient formaldehyde to convert them into the insoluble and infusible stage. The phenolic hydroxyl groups were sufficiently acidic to permit exchange with a wide variety of cations when solutions of the various salts were contacted with the resins. Acids were found to be suitable for regeneration of the resins, making cyclic operation possible.

Since the early work of Adams and Holmes ion-exchange resins have become an important segment of the chemical industry. Many types of resins have been developed to meet specific needs. Not only are both anion- and cation-exchange resins now available, but also resins have been designed for carrying out oxidation-reduction cycles²⁰⁶ and for the selective retention of products with specific functional groups, such as the sulfhydryl compounds.²⁰⁷ Ion-exchange resins have found many uses, including water softening, the removal and recovery of metals, acids, and bases, the deashing of organic compounds, the catalysis of wide variety of reactions, and in chromatography. Of the various resins available, the phenol-aldehyde resins have maintained a prominent place. A brief review of some of their more important modifications to make them suitable as ion-exchange materials is of interest.

Not long after the introduction of the phenol-aldehyde resins based on polyhydric phenols, it was found that resins containing carboxylic acid groups could be prepared that would function as ion-exchange materials. The carboxylic acid groups were introduced into the resins by the reaction of formaldehyde with mono- and polyhydroxybenzoic acids.^{201, 208} The substituted phenols were generally employed along with a sufficient quantity of a trifunctional phenol to give a thermoset resin.

Sulfonic acid groups, which have a strong affinity for basic ions, may be introduced into a phenol-aldehyde resin by several methods. Probably the least satisfactory procedure is to sulfonate a phenol-

aldehyde resin after it has been converted to the insoluble and infusible state. Another procedure is to react a phenolsulfonic acid with an aldehyde.^{201-208, 209} Enough phenol to give good curing properties to the resin is ordinarily added to the phenolsulfonic acid. An ion-exchange resin manufactured in Germany introduces the sulfonic groups by way of the aldehyde rather than through the phenol.²⁰⁸ For example, benzaldehyde-2,4-disulfonic acid is reacted with resorcinol. Formaldehyde is also used in the resin to improve its cure. As discussed in Chapter 6, products with sulfonic acid groups may be obtained by the reaction of phenols with formaldehyde and sodium sulfite or sodium bisulfite.²¹⁰⁻²¹² In this reaction the sulfonic group is attached by a methylene bridge to the phenol rather than directly to the ring of the phenol.

Anion-exchange resins based on phenol-aldehyde products are less common than the cation type. Probably the most widely used type of anion-exchange resin based on phenol is obtained by the reaction of phenol with formaldehyde in the presence of a primary amine.²¹² Such products will have both secondary and tertiary amine groups, depending on whether the amine has reacted once or twice. Both the secondary and tertiary amine groups are attached to the phenol through a methylene bridge. The reaction of nitromethane, phenol, and formaldehyde gives a resin containing nitro groups as an integral part of the resin. Upon reduction, a product with amine groups is formed which will function as an ion-exchange resin. Resins based on nitrophenols are also prepared and then reduced to give resins with amine groups.

The mercuration of phenol-aldehyde resins gives a product with a specific affinity for sulfhydryl compounds.²⁰⁷ The sulfhydryl compounds may be eluted from the resin by the action of dilute mercaptoethanol or hydrogen sulfide solutions.

Resins capable of chelating with various metals have been obtained by condensing formaldehyde with resorcinol and pyrogallolcarboxylic acid.²¹⁸

REFERENCES FOR CHAPTER 9

- ¹ K. Auwers, *Ber.*, **36**, 1878 (1903).
- ² A. W. Francis, *J. Am. Chem. Soc.*, **48**, 1631 (1926).
- ³ A. W. Francis and A. J. Hill, *Ind. Eng. Chem., Anal. Ed.*, **13**, 357 (1941).
- ⁴ M. M. Sprung, *Ind. Eng. Chem., Anal. Ed.*, **13**, 35-38 (1941).
- ⁵ M. M. Sprung, *J. Am. Chem. Soc.*, **63**, 334-343 (1941).
- ⁶ B. W. Nordlander, *Oil, Paint and Drug Repr.*, **130**, 3, 27 (Sept. 14, 1936).
- ⁷ J. Novak and V. Čech, *Ind. Eng. Chem.*, **20**, 796 (1928).
- ⁸ J. Novak and V. Čech, *Ind. Eng. Chem.*, **24**, 1275 (1932).

- ⁹ C. and L. Jacque, *Inds. plastiques*, 4, No. 1, 35-36 (1948).
- ¹⁰ H. von Euler and S. V. Kispeczy, *Z. physik. Chem.*, A189, 109 (1941).
- ¹¹ K. Oshima and E. Imoto, *Chem. High Polymers*, 3, 51-56 (1946).
- ¹² M. M. Sprung and M. T. Gladstone, *J. Am. Chem. Soc.*, 71, 2907-2913 (1949).
- ¹³ I. W. Ruderman, *Ind. Eng. Chem., Anal. Ed.*, 18, 753-759 (1946).
- ¹⁴ R. W. Martin, *J. Am. Chem. Soc.*, 73, 3952-3954 (1951).
- ¹⁵ H. S. Lilley and D. W. J. Osmond, *J. Soc. Chem. Ind.*, 66, 340-341 (1947).
- ¹⁶ R. H. Runk, *Ind. Eng. Chem.*, 42, 2110-2114 (1950).
- ¹⁷ H. F. Müller and I. Müller, *Kunststoffe*, 41, 186-188 (1951).
- ¹⁸ G. R. Sprengling, private communication.
- ¹⁹ K. Auwers, *Ann.*, 343, 192 (1905); *Ber.*, 40, 2524-2537 (1907).
- ²⁰ Th. Zincke, *Ann.*, 363, 246 (1908).
- ²¹ H. L. Bender, A. G. Farnham, and J. W. Guyer, U. S. pat. 2,464,207 (1950).
- ²² H. L. Bender and A. G. Farnham, U. S. pat. 2,475,587 (1949).
- ²³ Th. Zincke and M. Grueters, *Ann.*, 343, 85 (1905).
- ²⁴ K. Auwers and E. Rietz, *Ann.*, 356, 152-177 (1908).
- ²⁵ J. B. Niederl and R. N. Nagel, *J. Am. Chem. Soc.*, 63, 1235-1237 (1941).
- ²⁶ M. C. Hart and A. D. Hirschfelder, *J. Am. Chem. Soc.*, 42, 2678-2686 (1920).
- ²⁷ A. Zinke, *Plastics*, 1950, 289.
- ²⁸ K. Fries and F. Brandes, *Ann.*, 542, 48-77 (1939).
- ²⁹ E. Adler and S. Kyrining, *Svensk Kem. Tid.*, 53, No. 1, 5-11 (1940).
- ³⁰ E. Adler, S. Tingstam, and A. O. Caspersson, *Arkiv Kemi Mineral. Geol.*, B15, No. 10, 1-8 (1942).
- ³¹ F. Hanus and E. Fuchs (assisted by E. Ziegler), *J. prakt. Chem.*, (2), 152, 327-336 (1939).
- ³² H. von Euler, E. Adler, and B. Bergstrom, *Arkiv Kemi Mineral. Geol.*, B14, No. 25, 1-6 (1941).
- ³³ K. Auwers and E. Erklentz, *Ann.*, 302, 115 (1898).
- ³⁴ H. S. Lilley and D. W. J. Osmond, *J. Soc. Chem. Ind.*, 66, 425-427 (1947).
- ³⁵ S. Kyrning, *Arkiv Kemi Mineral. Geol.*, A15, No. 2, 1-9 (1941).
- ³⁶ E. Adler, H. von Euler, and H. G. Hasselquist, *Arkiv Kemi Mineral. Geol.*, B14, No. 24, 1-8 (1940).
- ³⁷ E. Ziegler and G. Zigeuner, *Kunststoffe*, 39, 191-192 (1949).
- ³⁸ E. Ziegler, I. Hontschik, and L. Milowiz, *Monatsh.*, 78, 334-342 (1948).
- ³⁹ A. Zinke, *J. Applied Chem.*, 1, pt. 6, 257-266 (1951).
- ⁴⁰ K. Auwers, *Ber.*, 32, 2987-3007 (1899).
- ⁴¹ K. Auwers and W. Hampe, *Ber.*, 32, 3005-3016 (1899).
- ⁴² K. Auwers and R. von Erggelet, *Ber.*, 32, 3016-3033 (1899).
- ⁴³ S. Van der Meer, *Rubber Chem. and Technol.*, 18, 853-873 (1945).
- ⁴⁴ Th. Zincke, *Ann.*, 343, 104-108 (1905).
- ⁴⁵ H. von Euler and H. Nystrom, *Arkiv Kemi Mineral. Geol.*, 14B, No. 26, 1-7 (1940).
- ⁴⁶ H. Einhorn, *Ann.*, 343, 244-245 (1905).
- ⁴⁷ K. S. Topchiev and V. I. Stavrovskaya, *Doklady Akad. Nauk S.S.S.R.*, 69, 193-195 (1949).
- ⁴⁸ V. I. Stavrovskaya and K. S. Topchiev, *Zhur. Obshchei Khim.*, 21, 525-532 (1951).
- ⁴⁹ K. Auwers and C. Kipke, *Ann.*, 343, 200 (1905).
- ⁵⁰ A. Zinke, G. Zigeuner, G. Weiss, and E. Wiesenberger, *Monatsh.*, 80, 160-169 (1949).

- ⁵² K. Auwers and F. Baum, *Ber.*, **29**, 2338-2348 (1896)
- ⁵² E. Ziegler and H. Lüdde, U. S. pat. 2,488,134 (1949).
- ⁵³ E. Ziegler and H. Lüdde, *Monatsh.*, **79**, 316-322 (1948)
- ⁵⁴ H. von Euler, E. Adler, H. Hasselquist, and M. Lundin, *Arkiv Kemi Mineral. Geol.*, **18A**, No. 7, 1-23 (1943).
- ⁵⁵ H. von Euler, E. Adler, and A. O. Caspersson, *Arkiv Kemi Mineral. Geol.*, **A16**, No. 11, 1-14 (1943).
- ⁵⁶ G. Zigeuner and E. Ziegler, *Monatsh.*, **79**, 100 (1948)
- ⁵⁷ K. Auwers and H. Traun, *Ber.*, **32**, 3309 (1899).
- ⁵² C. A. Buehler, R. L. Brown, J. M. Holbert, J. G. Fulmer, and G. W. Parker, *J. Org. Chem.*, **6**, 902-907 (1941).
- ⁵⁹ E. Ziegler and H. Lüdde, *Monatsh.*, **79**, 55-60 (1948)
- ⁶⁰ E. Ziegler, *Ber.*, **77**, 731-735 (1944).
- ⁶¹ C. L. Moyle and P. A. Wolfe, U. S. pat. 2,630,458 (1953)
- ⁶² M. Kohn and M. Jawetz, *Monatsh.*, **44**, 198 (1923).
- ⁶³ W. C. Harden and J. H. Brewer, *J. Am. Chem. Soc.*, **59**, 2379 (1937).
- ⁶⁴ M. Kohn and M. Jawetz, *Monatsh.*, **45**, 251 (1924).
- ⁶⁵ S. Van der Meer, *Rec. trav. chim.*, **63**, 147-156 (1944)
- ⁶⁶ S. Van der Meer, *Paper 48*, Rubber-stichting, Delft, Holland, 1944.
- ⁶⁷ G. Zigeuner and W. Schaden, *Monatsh.*, **31**, 1017-1023 (1950)
- ⁶⁸ J. Braun, *Liebigs Ann.*, **472**, 17 (1929).
- ⁶⁹ M. S. Kharasch and J. Porsche, *J. Org. Chem.*, **1**, 265 (1936-1937).
- ⁷⁰ A. Buroway and J. T. Chamberlain, *J. Chem. Soc.*, **1949**, 626-635.
- ⁷¹ E. Liebnitz and K. Nauman, *Chem. Technol.*, **3**, 5-10 (1951).
- ⁷² C. F. Gerhardt, *Ann. chim. phys.*, (3), **7**, 215 (1844).
- ⁷³ F. D. Chattaway and A. A. Morris, *J. Chem. Soc.*, **1927**, 2013-2017.
- ⁷⁴ A. Küntzel and M. Schwank, *Collegium*, **1940**, 441-455.
- ⁷⁵ D. M. Findlay, U. S. pat. 2,230,641 (1941).
- ⁷⁶ G. Ekström, *Svensk Kem. Tid.*, **62**, No. 4, 113-120 (1950).
- ⁷⁷ A. Zinke, F. Hanus, and E. Ziegler, *J. prakt. Chem.*, (2), **152** (1939).
- ⁷⁸ NG. PH. Buu-Hoi, D. Lavit, and NG. D. Xuong, *J. Chem. Soc.*, **1953**, 2612-2614.
- ⁷⁹ H. E. Faith, U. S. pat. 2,615,046 (1952).
- ⁸⁰ F. Ullmann and K. Brittner, *Ber.*, **42**, 2539-2548 (1909).
- ⁸¹ E. Ziegler and E. Gartler, *Monatsh.*, **80**, 634-638 (1949).
- ⁸² L. H. Baekeland, *J. Ind. Eng. Chem.*, **1**, 545-549 (1909).
- ⁸³ A. Vanscheidt, A. Itenberg, P. Erluikova, and G. Simonov, *Plasticheskie Massy*, No. 3, **1934**, 17-25.
- ⁸⁴ A. Vanscheidt, A. Itenberg, and G. Shtraikhman, *Narodnyi Komissariat Tyazhoeloi Prom. S.S.S.R.*, *Sbornik*, **2**, 145-159 (1937).
- ⁸⁵ V. Wagner, *J. prakt. Chem.*, (2), **65**, 313 (1902).
- ⁸⁶ R. Barthel, *J. prakt. Chem.*, **161**, 77-80 (1942).
- ⁸⁷ R. Barthel, *Plastica (Holland)*, **2**, 247-251 (1949).
- ⁸⁸ R. Barthel, *Ber.*, **76**, 573-574 (1943).
- ^{88a} J. D. Head, U. S. pat. 2,639,298 (1953).
- ⁸⁹ K. Auwers, *Ann.*, **356**, 124, 128 (1907).
- ⁹⁰ S. Kyrning, *Arkiv Kemi Mineral. Geol.*, **B15**, No. 11, 1-8 (1941).
- ⁹¹ M. Jacobson, *Kunststoffe*, **11**, 105-106 (1921).
- ⁹² H. A. Bruson, U. S. pat. 2,265,141 (1942).
- ⁹³ H. A. Bruson and C. W. MacMullen, *J. Am. Chem. Soc.*, **63**, 270-272 (1941).

- ⁹⁴ H. A. Bruson, U. S. pat. 2,218,739 (1940).
⁹⁵ A. Zinke and St. Pucher, *Monatsh.*, 79, 26-41, (1948).
⁹⁶ E. Ziegler and G. Zigeuner, *Monatsh.*, 79, 42-54 (1948).
⁹⁷ F. Hanus, *J. prakt. Chem.*, 155, 317-331 (1940).
⁹⁸ F. Hanus, *J. prakt. Chem.*, 158, 254-265 (1941).
⁹⁹ F. Elger, U. S. pat. 1,965,458.
¹⁰⁰ D. M. Al'vin-Gutzats, V. A. Ivanov, et al., U. S. S. pat. 65,996 (1946).
¹⁰¹ L. N. Ferguson, *Chem. Revs.*, 38, 231 (1946).
¹⁰² W. L. Faith, D. B. Keyes, and R. L. Clark, *Industrial Chemicals*, John Wiley & Sons, 1950.
¹⁰³ G. C. Helintzer and B. Rodnevich, *J. Applied Chem. U.S.S.R.*, 8, 909 (1935).
¹⁰⁴ J. B. Fishman, *J. Am. Chem. Soc.*, 42, 2297-2302 (1920).
¹⁰⁵ J. B. Fishman, *J. Am. Chem. Soc.*, 42, 2288-2297 (1920).
¹⁰⁶ K. H. Meyer, *Trans. Faraday Soc.*, 82, 345 (1936).
¹⁰⁷ G. R. Sprengling and J. H. Freeman, *J. Am. Chem. Soc.*, 72, 1982-1985 (1950).
¹⁰⁸ R. W. Martin, Preprint *Bull., Div. Paint, Varnish, and Plastics Chem.*, American Chemical Society Meeting, Chicago, 1950, pp. 68-72.
¹⁰⁹ F. Seebach, *Ber.*, 73, 1338 (1940).
¹¹⁰ K. Auwers and E. Ziegler, *Ber.*, 29, 2348-2355 (1896).
¹¹¹ Y. Nakamura, *J. Chem. Soc. Japan*, 54, 167 (1951).
¹¹² A. Steiner, *Ber.*, 9, 287-289 (1878).
¹¹³ R. W. Hall, *Chemistry & Industry*, 28, 683 (1952).
¹¹⁴ H. A. Bruson and R. F. McCleary, U. S. pat. 2,220,835 (1940).
¹¹⁵ E. Ziegler and I. Simmler, *Ber.*, 74B, 1871-1879 (1941).
¹¹⁶ E. Ziegler, H. Meralla, and I. Simmler, *Ber.*, 76, 664-669 (1943).
¹¹⁷ C. A. Buehler, B. C. Bass, R. B. Darling, and M. E. Lubs, *J. Am. Chem. Soc.*, 62, 890 (1940).
¹¹⁸ C. A. Buehler, G. F. Deebel, and R. Evans, *J. Org. Chem.*, 6, 216 (1941).
¹¹⁹ W. Borsche and A. D. Berkhout, *Ann.*, 330, 82 (1904).
¹²⁰ Y. Nakamura, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 55, 85-87 (1952).
¹²¹ K. Sestanj, *Arhiv Kem. i. Technol.*, 23, 80-81 (1951).
¹²² J. C. Sheehan and G. D. Laubach, *J. Am. Chem. Soc.*, 72, 2478-2481 (1950).
¹²³ C. E. Frank, U. S. pat. 2,478,261 (1949).
¹²⁴ R. Boehm, *Ann.*, 318, 253 (1898); 329, 269, 301 (1903).
¹²⁵ K. Fries and E. Hübner, *Ber.*, 39, 435 (1906).
¹²⁶ J. J. Sleightholme, *Varnish Making*, Chemical Publishing Co., New York, 1940, p. 86.
¹²⁷ H. I. Waterman and A. R. Veldman, *Brit. Plastics*, 8, 125-128, 182-184 (1936).
¹²⁸ C. A. Buehler, D. E. Cooper, and E. O. Scrudder, *J. Org. Chem.*, 8, 316 (1943).
¹²⁹ R. S. Finn, G. J. Lewis, and N. J. L. Megson, *J. Soc. Chem. Ind.*, 69, Supp. Issue 2, S51-S53 (1950).
¹³⁰ A. C. Davis, B. T. Hayes, and R. F. Hunter, *J. Applied Chem.*, 3, Pt. 7, 312 (1953).
¹³¹ A. T. Carpenter and R. F. Hunter, *J. Applied Chem.*, 1, Pt. 5, 217-226 (1951).
¹³² J. H. Burckhalter, *J. Am. Chem. Soc.*, 72, 5309-5310 (1950).

- 133 S. R. Finn, et al., *J. Applied Chem.*, 1, Pt. 11, 524-526 (1951); 2, 88-90 (1952).
- 134 W. J. Burke, Armed Services Tech. Infor. Agency, AD-6855 and AD-12801.
- 135 T. Kennedy, *Chemistry & Industry*, 1940, 297.
- 136 W. T. Caldwell and T. R. Thompson, *J. Am. Chem. Soc.*, 61, 765-767 (1939).
- 137 W. Reeve and A. Saddle, *J. Am. Chem. Soc.*, 72, 3252 (1950).
- 138 H. A. Bruson and L. W. Covert, U. S. pat. 2,194,215 (1940).
- 139 W. J. Moran, E. C. Schreiber, E. Engel, D. C. Behn, and J. L. Yamins, *J. Am. Chem. Soc.*, 74, 127 (1952).
- 140 R. C. Carlin and H. P. Landerl, *J. Am. Chem. Soc.*, 72, 2762-2763 (1950).
- 141 J. W. Cornforth, R. H. Cornforth, and R. Robinson, *J. Chem. Soc.*, 1942, 682.
- 142 H. Rapoport, T. P. King, and J. B. Lavinge, *J. Am. Chem. Soc.*, 73, 2718 (1951).
- 143 S. R. Finn and J. W. G. Musty, *Chemistry & Industry*, 1950, 677.
- 144 S. R. Finn and J. W. G. Musty, *J. Applied Chem.*, 1, 182-184 (1951).
- 145 J. Reese, *Angew. Chem.*, 64, 399-400 (1952).
- 146 J. H. Freeman, *J. Am. Chem. Soc.*, 74, 6257 (1952).
- 147 J. C. Duff and V. I. Furness, *J. Chem. Soc.*, 1951, 1512-1515.
- 148 S. Van der Meer, *Kunststoffe*, 37, 41 (1947).
- 149 A. Buroway and J. T. Chamberlain, *J. Chem. Soc.*, 1949, 624-626.
- 150 K. Hultsch, *Kunststoffe*, 39, 57-63 (1949).
- 151 K. Hultsch, *Kunststoffe*, 39, 192 (1949).
- 152 A. Greth, *Angew. Chem.*, 51, 719 (1938).
- 153 W. Krumbhaar, U. S. pat. 2,268,946 (1942).
- 154 I. W. Ruderman and E. M. Fettes, *J. Am. Chem. Soc.*, 71, 2264 (1949).
- 155 R. F. McCleary and S. M. Roberts, U. S. pat. 2,322,376 (1943).
- 156 P. W. Neber and P. Kubitzky, Dissertation by P. Kubitzky, Tübingen, 1937.
- 157 F. Zipples, Dissertation, Tübingen, 1939.
- 158 G. Zigeuner and E. Ziegler, *Monatsh.*, 79, 89 (1948).
- 159 E. Ziegler and G. Zigeuner, *Monatsh.*, 79, 358-362 (1948).
- 160 E. Ziegler and G. Zigeuner, *Monatsh.*, 79, 363-370 (1948).
- 161 G. Zigeuner and E. Ziegler, *Monatsh.*, 79, 371-378 (1948).
- 162 E. Ziegler, G. Zigeuner, and A. Kainzner, *Monatsh.*, 80, 295-302 (1949).
- 163 G. Zigeuner and E. Ziegler, *Monatsh.*, 80, 359-363 (1949).
- 164 G. Zigeuner, E. Ziegler, and F. Aspan, *Monatsh.*, 81, 480-487 (1950).
- 165 K. Brass and P. Sommer, *Ber.*, 61, 993 (1928).
- 166 R. Mohlau and E. Strohbach, *Ber.*, 33, 804 (1900).
- 167 E. Marder and I. W. Ruderman, *J. Am. Chem. Soc.*, 73, 5475-5476 (1951).
- 168 E. Ziegler et al., *Monatsh.*, 82, 238-244 (1951); 84, 287-290 (1953).
- 169 J. H. Freeman, *Anal. Chem.*, 24, 955, 2001 (1952).
- 170 E. Ziegler and K. Gartler, *Monatsh.*, 79, 637-638 (1948).
- 171 E. Ziegler, K. Gartler, and E. Wiesenberger, *Monatsh.*, 80, 759-764 (1949).
- 172 R. W. Martin, U. S. pats. 2,579,329 (1951); 2,579,330 (1951); 2,579,331 (1951).
- 173 R. W. Martin, Div. Polymer Chemistry, American Chemical Society Meeting, Atlantic City, September, 1952.
- 174 E. F. Pratt and J. D. Draper, *J. Am. Chem. Soc.*, 71, 2846-2849 (1949); E. F. Pratt, R. K. Preston, and J. D. Draper, *J. Am. Chem. Soc.*, 72, 1367-1369 (1950).

- 175 M. J. Rhoad and P. J. Flory, *J. Am. Chem. Soc.*, **72**, 2216-2219 (1950).
176 A. Greth, *Kunststoffe*, **31**, 345 (1941).
177 S. M. Gerber and D. Y. Curtin, *J. Am. Chem. Soc.*, **71**, 1499 (1949).
178 R. W. Martin, *J. Am. Chem. Soc.*, **74**, 3024-3025 (1952).
179 M. DeGroote and B. Keiser, U. S. pats. 2,499,368 (1950); 2,499,361 (1950).
180 L. H. Bock and J. L. Rainey, U. S. pat. 2,504,064 (1950).
181 P. Castan, U. S. pat. 2,324,483 (1948).
182 P. Castan, U. S. pat. 2,444,333 (1948).
183 H. L. Bender, A. G. Farnham, and J. W. Guyer, U. S. pat. 2,506,486 (1950).
184 S. O. Greenlee, U. S. pat. 2,494,295 (1950).
185 R. W. Martin, U. S. pats. 2,606,934 (1952); 2,606,935 (1952).
186 B. Becker and E. Barthel, *Monatsh.*, **79**, 216-222 (1948).
187 J. L. Brannon, U. S. pat. 2,475,005 (1949).
188 T. Backhouse, A. McGookin, J. Matchet, A. Robertson, and E. Tittensor, *J. Chem. Soc.*, **1948**, 113-115.
189 A. McGookin, A. Robertson, and T. H. Simpson, *J. Chem. Soc.*, **1951**, 2021-2029.
190 A. T. Carpenter and R. F. Hunter, *J. Chem. Soc.*, **1954**, 2731.
191 M. G. Barclay, A. Buroway, and C. H. Thomson, *J. Chem. Soc.*, **1944**, 400-404.
192 S. R. Finn, G. J. Lewis, and N. J. L. Megson, *J. Soc. Chem. Ind.*, **69**, 129-132 (1950).
193 J. B. Niederl, V. Niederl, S. Skapiro, and M. E. McGreal, *J. Am. Chem. Soc.*, **59**, 1113-1115 (1937); **61**, 345-348 (1939).
194 J. L. Jones, U. S. pat. 2,587,578 (1952).
195 E. Adler, H. von Euler, and G. J. Gie, *Arkiv Kemi Mineral. Geol.*, **A16**, No. 12, 1-20 (1943).
196 D. R. May, K. W. Saunders, E. L. Kropa, and J. K. Dixon, *Discussions of Faraday Soc.*, No. 8, 290-296 (1950).
197 M. G. Sturrock and T. Lawe, U. S. pat. 2,373,982 (1945).
198 R. Kunin and R. J. Myers, *Ion Exchange Resins*, John Wiley & Sons, New York, 1950.
199 D. S. Herr in Carswell, *Phenoplasts, Their Structure, Properties and Chemical Technology*, Interscience Publishers, New York, 1947, Chapter XIV.
200 N. K. Hiester and R. C. Phillips, *Chem. Eng.*, **61**, No. 10, 161-180 (1954).
201 W. C. Bauman, *Ind. Eng. Chem.*, **38**, 46 (1946).
202 T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, **1949**, 1190-1213.
203 G. Moralli, *Compt. rend.*, **232**, 332-334 (1951).
204 B. A. Adams and E. L. Holmes, *J. Soc. Chem. Ind.*, **54**, 1-6 (1935).
205 B. A. Adams and E. L. Holmes, Brit. pats. 450,308-9 (1936); 474,361 (1937); U. S. pats. 2,104,501 (1938); 2,151,883 (1939); 2,191,853 (1940).
206 H. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 402 (1949).
207 H. T. Miles, E. R. Stadtman, and W. W. Kielley, *J. Am. Chem. Soc.*, **76**, 4041 (1954).
208 B. I. O. S. Report 621, Item 22 (1946).
209 D. M. Findlay, U. S. pat. 2,230,641 (1941).
210 E. L. Holmes, U. S. pat. 2,191,853 (1940).
211 D. M. Day and R. L. DeHoff, U. S. pat. 2,522,569 (1950).
212 W. C. Bauman in Nachod, *Ion Exchange*, Academic Press, New York, 1949.
213 J. R. Parrish, *Chemistry & Industry*, **14**, 387 (1955).

C H A P T E R T E N

Reaction Kinetics

Rate studies of the phenol-aldehyde reaction have been of two types. In the first group are those that are largely empirical. Under this heading fall measurements on the changes in resin viscosity,¹⁻⁸ density,^{1,2,9,10} refractive index,^{8,11-14} cloud point,¹⁸ resinification or gelation time,^{1,16-19} and solubility.^{10,20-21} As the resin cures, changes in conductivity or dielectric constant,^{8,22-28} hardness or strength,²⁸ solvent resistance or swelling by solvents,²⁷⁻²⁹ and loss in weight give a rough estimate of the progress of cure. Though changes such as those listed above are manifestations of the various chemical reactions in progress during the preparation and cure of a phenolic resin, they do not lend themselves to detailed interpretation on a kinetic basis. Opposed to the studies of the changes in gross properties of the phenol-aldehyde condensates have been those where quantitative data on the disappearance of individual reactants have been collected and interpreted. This discussion will be devoted to the consideration of data of that type.

Ideally, kinetic studies should be run with a wide variation in the ratio of reactants and catalyst concentration. If a large excess of one reactant is used one achieves the effect, for kinetic purposes, of holding one reactant constant while following the disappearance of the other reactants. It is also desirable to run the reactions in dilute solution. However, in order to make the data more directly comparable to manufacturing practice most of the studies of the phenol-formaldehyde reaction have been run in fairly concentrated solutions with formaldehyde-to-phenol ratios and catalyst concentrations close, if not equal, to those used in actual commercial practice.

As already discussed in Chapter 4 the formation of a phenol-aldehyde resin involves a series of stepwise reactions, all of which are susceptible of catalysis by acidic and basic materials. The first phase of the reaction involves the addition of formaldehyde to a phenol to form a phenol alcohol. As this reaction may occur more than once

with polyfunctional phenols, phenol polyalcohols may result. The second phase of the reaction is the condensation of the phenol alcohols to form higher-molecular-weight methylene or dibenzyl ether derivatives. A third phase involving fundamental changes in the polymeric products at high temperatures is recognized but is not of interest to the present discussion.

The over-all course of the phenol-formaldehyde reaction is strongly dependent on the type as well as on the amount of catalyst employed. Most acidic materials appear to function in a similar manner to give predominantly methylene derivatives. However, major differences in the properties of the resins obtained are noted depending on the choice of alkaline catalyst. Strong alkalis cause a very rapid addition of methylol groups but are less effective, although still active, in bringing about their condensation to higher-molecular-weight products. For this reason these catalysts are selected when it is desirable to tie in a lot of formaldehyde or prepare a water-dilutable resin. Unlike the strong alkalis, ammonia and certain amines, although basic, cause a rapid loss in water solubility. Yet by their use more than a mole of formaldehyde may be combined with a mole of phenol and a satisfactory heat-convertible resin may be obtained which is not readily formed with an acidic catalyst. The ultimate course of the reaction with any catalyst is obviously a function of the rates at which the addition and condensation reactions proceed in the presence of that catalyst. In order to simplify the presentation the effect of each type of catalyst on these two major types of reactions will be considered separately.

The most serious problem in obtaining data on the phenol-formaldehyde reaction suitable for kinetic treatment has been the development of adequate analytical tools for following the progress of the various reactions in such a complex system. Of the initial reactants formaldehyde is most readily determined, and most studies have been based on its measurement. Several procedures are available for the determination of formaldehyde in the presence of phenolic materials.³⁰⁻³² One of the simplest methods involves titration with hydroxylamine-hydrochloride according to Gambier as modified by Nordlander.^{32, 33}

The determination of unreacted phenol in a phenol-formaldehyde reaction mixture has proved difficult because of the close similarity in structure and reactions of phenol to the early condensation products. Although it is possible to remove phenol from a phenol-aldehyde reaction mixture by steam distillation, the process is slow and cumbersome and does not lend itself to use in rate studies.³⁴⁻³⁵ There is also some question that conditions may be achieved that will permit dis-

tillation of the phenol without bringing about further reaction. Saligenin is also slightly volatile with steam. However, in spite of the drawbacks the technique has found some use. Another method for determining phenol in the presence of other phenolic materials, such as the phenol alcohols and dihydroxydiphenylmethanes, is based on infrared absorption. The method was developed by Smith, Rugg, and Bowman³⁷ and would appear to be ideally suited for rate studies, but its use in this capacity has not been reported. Freeman^{38,39} has developed a technique based on paper chromatography for determining not only the free phenol but also the various phenol alcohols in a phenol-formaldehyde reaction mixture. The technique, also used with some modification by Imoto et al.,^{40,41} has proved highly successful in rate studies. Other procedures for estimation of phenol also have been reported.^{42,43}

The earliest attempts at following the resinification step depended on the difference in solubility of the initial reaction products, the phenol alcohols, and the resin molecules. Some workers have utilized the appearance of a permanent cloudiness in a reaction mixture as an indication of the onset of resinification; others have diluted samples of the reaction mixture with a water-miscible solvent and then titrated with a non-solvent for the resin, such as water, to the point of cloudiness.^{13,20,44} The latter method permitted following the resinification reaction over a considerable portion of the reaction period, as opposed to the first method, where a single point reading is obtained. Still others have used the temperature at which clouding of the reaction mixture sets in.^{15,45,46} As resinification proceeds, the temperature at which turbidity appears becomes higher.

All the techniques mentioned above suffer from the same weakness in that comparison between phenols is difficult because of the inherent differences in solubility of the various phenols and their condensation products. The methods also have the fault of telling only when a portion of the material in the reaction mixture is no longer soluble therein. Turbidity or cloudiness is caused by saturation of the reaction mixture to a certain component or group of components and presumably may be achieved by either a small amount of a high-molecular-weight fraction or a relatively large amount of a lower-molecular-weight fraction. Unless the precipitated portion is separated and its average molecular weight determined there is no means of knowing which is true.

A better procedure is to follow the resinification step by chemical means. This was first attempted by measuring the decrease in the "bromine number" of the reaction mixture or of a water-soluble portion

thereof.^{11-13,47-50} This technique is based on the observation that *o*- and *p*-hydroxybenzyl alcohol react with acidified bromate-bromide solution as if the methylol groups were absent whereas their condensation products lose one position reactive towards bromine for each phenol ring involved in a condensation reaction. By knowing the amount of formaldehyde consumed and the bromine number of the reaction mixture it becomes possible, at least theoretically, to determine the extent of the condensation reactions. Unfortunately the polymethylol derivatives of phenol, formed in particular with higher ratios of formaldehyde to phenol, or the phenol alcohols derived from alkyl phenols do not behave ideally. With the substituted phenol alcohols, overbromination may occur by reaction in the side chain or at the methylene bridge of the condensed products, and with the polymethylol derivatives of phenol the methylol groups are not removed quantitatively. However, in spite of these limitations, measurements of the bromine number of a phenol-formaldehyde reaction mixture have been employed by several workers with interesting results.^{12, 48, 51-56} The main risk in using the data lies not in the general conclusion drawn but in attaching absolute significance to the numerical values obtained, particularly with the alkyl phenols.

Methods have also been announced for the direct determination of the total methylol content of phenol-aldehyde condensates as well as the over-all reactivity of a phenolic resin that might possess methylol, dibenzyl ether, or benzylamine groups.^{57, 58}

A. ADDITION REACTION

Strong Alkalies

The formation of phenol alcohols by the addition of formaldehyde to a phenol is strongly catalyzed by strong alkalies such as sodium hydroxide, barium hydroxide, calcium hydroxide, sodium carbonate, and quaternary ammonium hydroxides. With such catalysts some difficulty was experienced at first in finding a rate expression that accurately described the disappearance of the formaldehyde during the entire course of the reaction. Jones⁵⁹ reported that at a *pH* of 8.5 a first-order rate law was followed for approximately 45% of the reaction. This interpretation has been criticized by Goldblum,⁶⁰ who contends that the data show better conformity to a second-order rate expression. Debing, Murray, and Schatz⁴⁸ found that their data would fit neither a conventional first- nor a second-order rate expression. As is the general practice, tests for conformity to first- and second-order kinetics were made by plotting respectively $\log a/(a - x)$

vs. time and $x/(a - x)$ vs. time, where a is the initial concentration of formaldehyde and x is the amount reacted at time t . In the first case curves were obtained that sloped downward from a straight line; in the second case the plot of the data drifted upward from a straight line. The data were then tested in certain modified expressions. The final expression took the form

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - 2x)}{a(b - 2x)}$$

To test this equation the expression $\log \frac{b(a - 2x)}{a(b - 2x)}$ was plotted against time. The plots using this expression exhibited conformity for the entire reaction period with various ratios of phenol to formaldehyde as well as with different catalyst concentrations and at different temperatures. The rate expression applies not only when sodium hydroxide is the catalyst but also when primary, secondary, or tertiary amines or quaternary ammonium hydroxides are used. The rate constants for the tertiary amine and the quaternary ammonium hydroxides are close to those for sodium hydroxide while those for mono- and diethylamine are much lower. (See Table I, where the rate constants for the amine

Table I

Catalyst	$K \times 10^6$ (kg./mole sec.)
Sodium hydroxide	19.4
Monoethylamine	5.0
Diethylamine	6.4
Triethylamine	17.6
Tetraethyl ammonium hydroxide	22.2

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and caustic catalyzed reactions are given.) The constants were determined with 0.05 mole of catalyst at 80°C.

Interpretation of the above rate expression according to any reaction sequence is difficult. In order to derive the expression it was assumed that two reactive positions were removed from both the phenol and formaldehyde for each methylol group formed. It is not readily apparent why this should be true. This point is particularly troublesome when one considers that the addition of a methylol group to certain phenols accelerates the addition of more formaldehyde (2,6-di-

methylophenol is more reactive than saligenin). It is also surprising that the same rate expression should describe the disappearance of the formaldehyde equally well when the catalyst is a primary, secondary, or tertiary amine or a quaternary ammonium hydroxide. The primary and secondary amines in themselves are capable of reaction with formaldehyde; the other catalysts are not.

The major difficulty in attempting to correlate the rate data on the disappearance of formaldehyde with a reaction sequence is that the data represent a summation of reactions and not a single reaction. Since phenol has three reactive positions, methylol groups are conceivably being added not only to the starting phenol but, after the reaction has been in progress for a time, to both phenol mono and phenol dialcohols as well. An excellent solution to this problem has been provided by Freeman and Lewis³⁹ for the reaction catalyzed by caustic and with 3 moles of formaldehyde per mole of phenol. The paper by Freeman and Lewis is one of the most significant yet to appear dealing with the kinetics of the addition of formaldehyde to phenols. It is hoped their technique will be extended to other catalysts and to other mole ratios of phenol to formaldehyde.

By means of paper chromatography, Freeman and Lewis have been able to follow quantitatively both the appearance and disappearance of each individual methylophenol in a phenol-formaldehyde reaction. Mathematical analysis of the data from separate experiments involving phenol and each of the four phenol alcohols capable of reacting further with formaldehyde gave individual rate constants for each of the phenol alcohols and for phenol. It will be noted that all reactions were of second order. The various reactions and rate constants involved in going from phenol to trimethylophenol are shown in Fig. 5.

Data typical of those obtained by Freeman and Lewis³⁹ are shown in Table II, where the reaction of phenol with formaldehyde was studied. Table III gives the relative reactivities of the nuclear positions for the various phenol alcohols with *p*-methylophenol serving as the reference phenol.³⁹ It is readily seen from an inspection of Table III why the earlier workers had difficulty in finding rate expressions that would adequately describe the over-all reaction of formaldehyde with phenol.

From the data on the relative reactivities of the various methylophenols the authors also have made predictions as to the course of the reaction where less than 3 moles of formaldehyde per mole of phenol is used. It was thought that saligenin would be the first product formed in appreciable quantity. Its concentration in the reaction

mixture, after an early increase, would then remain essentially constant for some time since its rate of further reaction would be about as great as its rate of formation. It would be the first phenol alcohol to disappear as reaction continued. *p*-Methylolphenol would appear later than the *ortho* isomer, but it would increase in concentration as the reaction proceeded. 2,4-Dimethylolphenol would appear still later and would, owing to its low reactivity, become a major constituent of the reaction mixture. On the other hand, 2,6-

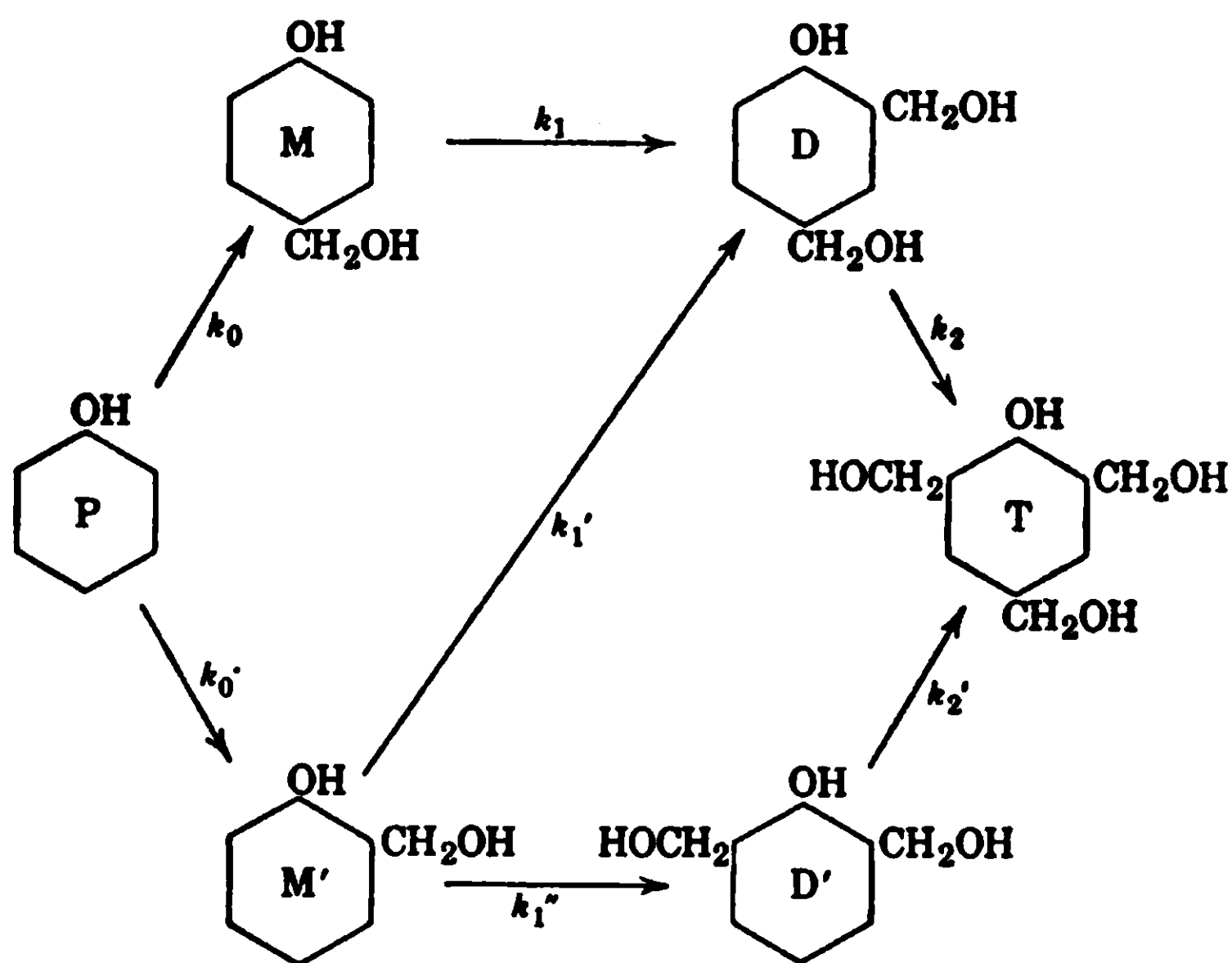


Fig. 5. Reprinted by permission of the authors, J. H. Freeman and C. W. Lewis, and by permission of the editor of *J. Am. Chem. Soc.*

dimethylolphenol, because of its very high reactivity, would never be found in large quantity. These predictions are in general agreement with the results obtained by Sprengling and Freeman by analysis of a reaction mixture obtained with 1.4 moles of formaldehyde per mole of phenol.⁴⁰

Figure 6 summarizes the results on the appearance and disappearance of the various phenol alcohols when 3 moles of formaldehyde are used per mole of phenol.³⁹

The effect of methylol substitution on the over-all rate of formaldehyde consumption also has been analyzed by Freeman and Lewis.³⁹ As methylol substitution proceeds, the apparent reactivity of the system, phenol plus formaldehyde, clearly increases. This increased reactivity of the system is caused by the formation of saligenin and

Table II. Alkaline Reaction of Phenol + 3 Formaldehyde at 30°C.

Concentration (mole/liter) of Components with Time							
Hrs	Phenol (calculated)	Saligenin	p-Hydroxy- benzyl Alcohol	2,6-Di- methylol- phenol	2,4-Di- methylol- phenol	2,4,6-Tri- methylol- phenol	Tetra- methylol- p,p'-Ditan *
0	0.1804	—	—	—	—	—	—
0.1	.1536	0.0160	0.0090	—	—	—	—
0.3	.1477	.0210	.0177	—	—	—	—
0.5	.1373	.0248	.0183	Trace	Trace	—	—
0.75	.0089	.0303	.0228	0.0065	0.0141	0.0078	—
1.0	.0829	.0362	.0276	.0072	.0188	.0078	—
1.5	.0753	.0308	.0289	.0088	.0249	.0117	—
2.0	.0638	.0308	.0317	.0083	.0288	.0170	—
3.5	.0240	.0261	.0344	.0130	.0418	.0402	—
5.0	.0061	.0210	.0302	.0120	.0446	.0665	—
6.5	—	.0203	.0256	.0109	.0549	.0950	—
8.0	—	.0174	.0220	.0101	.0579	.1028	—
12	—	.0127	.0153	.0098	.0525	.1258	—
23	—	—	.0112	—	.0337	.1455	—
30	—	—	.0079	—	.0309	.1604	Trace
47	—	—	.005	—	.0247	.1650	Trace
55	—	—	Trace	—	.0256	.1648	0.0137
72	—	—	—	—	.0184	.1540	.0157
100	—	—	—	—	.0172	.1518	.0249
167	—	—	—	—	—	.1369	.0218
200	—	—	—	—	—	.1259	.0273
270	—	—	—	—	—	.1150	.0327
340	—	—	—	—	—	.0989	.0407
440	—	—	—	—	—	.0902	.0451
510	—	—	—	—	—	.0848	.0478
680	—	—	—	—	—	.0751	.0362

* Ditan = dihydroxydiphenylmethane.

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Table III. Reactivity of Individual Nuclear Positions in Methylol-phenols

Compound	Position Relative to Phenolic Hydroxyl	Relative Reactivity
<i>p</i> -Hydroxybenzyl alcohol	<i>ortho</i>	1.0
Phenol	<i>ortho</i>	1.4
Phenol	<i>para</i>	1.7
Saligenin	<i>para</i>	2.0
Saligenin	<i>ortho</i>	2.3
2,4-Dimethylolphenol	<i>ortho</i>	2.4
2,6-Dimethylolphenol	<i>para</i>	11.1

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2,6-dimethylolphenol, both of which are more reactive with formaldehyde than phenol. The rate of reaction eventually levels off and approaches that of 2,4-dimethylolphenol, the last remaining component of the system that is reactive with formaldehyde.

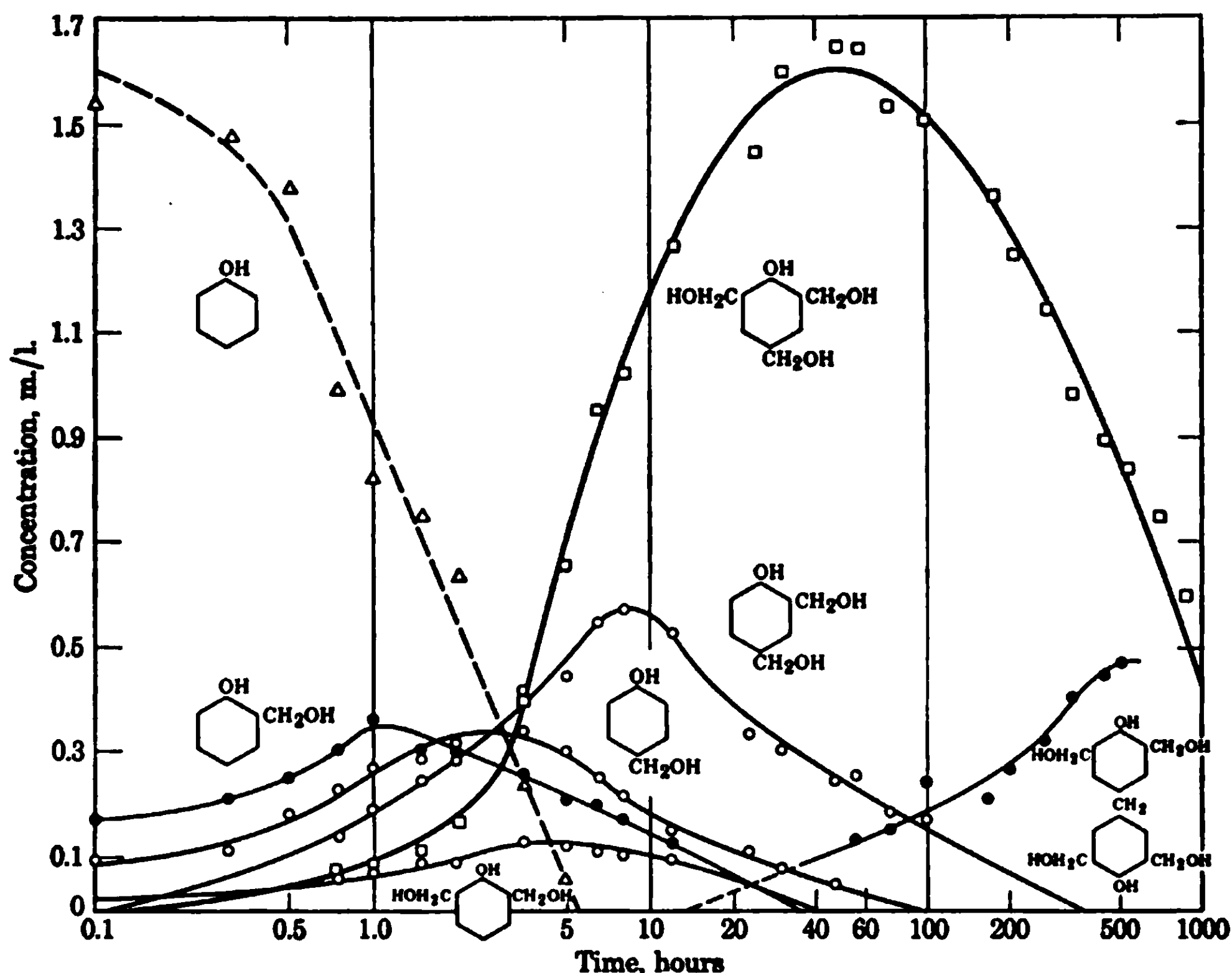


Fig. 6. Phenol + formaldehyde (NaOH, 30°), concentration vs. log time. Reprinted by permission of the authors, J. H. Freeman and C. W. Lewis, and by permission of the editor of *J. Am. Chem. Soc.*

A number of other investigations of the addition of formaldehyde to phenols in the presence of caustic have been made.⁶¹⁻⁶⁴ Stults, Moulton, and McCarthy,⁶⁵ who studied the reaction of aqueous sodium *p*-hydroxyphenylsulfonate with formaldehyde, found that the reaction followed second-order kinetics as judged from the rate of disappearance of the formaldehyde.

DeJong and DeJonge⁶⁴ made a detailed study of the hydroxymethylation of phenols in the *pH* range 1-11 and between 70° and 130°C. in dilute aqueous solution. The rate constants are found by taking the tangent of the conversion plot at zero time. The rate expression is

$$(dF/dt)_{t=0} = K[P]_0^m[F]_0^n$$

where $[P]_0$ and $[F]_0$ are the initial concentrations of phenol and formaldehyde. It was concluded that the reaction was bimolecular since the initial rates were nearly proportional to the concentration of both reactants. The rate of reaction was found to be directly proportional to the hydroxyl-ion concentration above a pH of 5 and up to approximately 1 mole of caustic per mole of phenol. A minimum

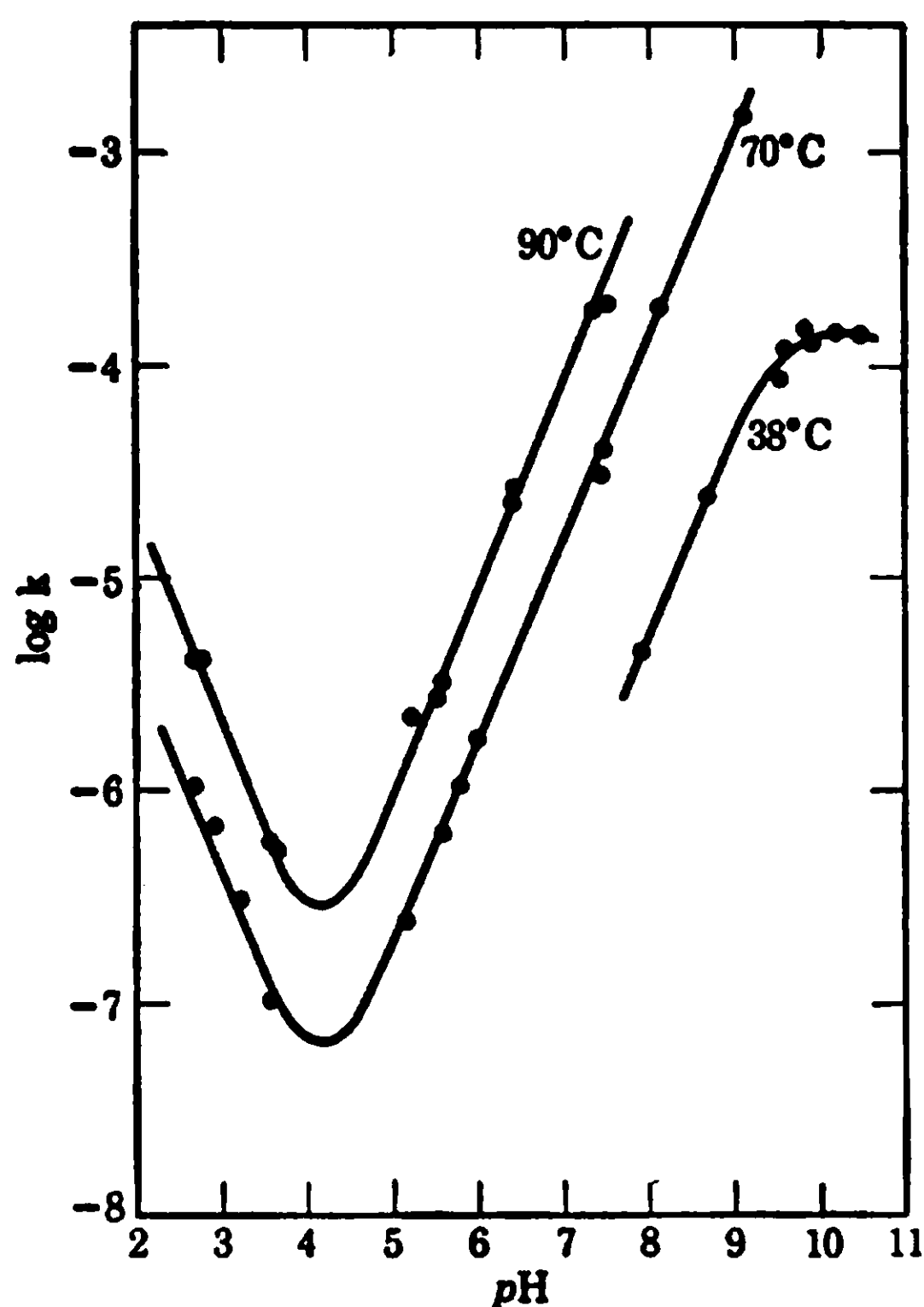


Fig. 7. Reprinted from *Travaux du Colloque International sur l'hydroxycarbon-ylation*, Gault, Paris, 31 May–5 June, by permission of the authors, J. I. deJong and J. deJonge, and by permission of G. Kersaint, Redacteur en Chef du *Bulletin*.

in rate was found at a pH around 4; below this, the reaction shifted to one catalyzed by acids (see Fig. 7). With a molar excess of caustic, little increase in the rate of reaction was observed, presumably because the quantity of phenol present as phenate ion changed very slowly after the equivalent point had been reached. Aqueous triethanolamine also gave a second-order reaction exclusively dependent on the hydroxyl-ion concentration. Buffers and salts were without effect on the rate of reaction. An activation energy of 22 kcal./mole was found.

Vanscheidt⁶⁶ has made a detailed study of the initial stages of the phenol-formaldehyde reaction using a slight excess of formaldehyde

over the phenol, with sodium, calcium, and barium hydroxide as catalysts. At temperatures below about 50°C. only the addition reaction was important. With formalin as a source of formaldehyde, non-viscous solutions were formed which contained approximately 35% water, 15% unreacted phenol, and 50% of the simple phenol alcohols, e.g., saligenin, *p*-hydroxybenzyl alcohol and the bis(hydroxymethyl)-phenols. These solutions were soluble in water in all proportions and underwent resinification on heating at 80–100°C.

Analysis of the reaction mixtures at regular intervals showed that sodium, calcium, and barium hydroxide do not have the same catalytic effect on the addition reaction. Both at 22° and 50°C., with a ratio of formaldehyde to phenol of 1.1 to 1, and also at a ratio of 1.4 to 1, the rate with calcium hydroxide was much higher than with the other bases. For example, at 22°C. all the formaldehyde was consumed in 8 days with 3% calcium hydroxide as catalyst whereas with the same amount of sodium hydroxide 20 days was required to cause all the formaldehyde to react. Barium hydroxide was even less effective on a weight basis. This might be predicted since barium hydroxide has a higher molecular weight and therefore fewer equivalents of catalyst would be present. However, with calcium and sodium hydroxide the equivalent weights are very close. An adequate explanation for the enhanced reactivity of calcium hydroxide has not been given.

Vanscheidt also presented some very interesting data on the relative rates of disappearance of the phenol and formaldehyde in a typical reaction mixture.^{66,66} After 12 hours at 50°C., for example, with a phenol-to-formaldehyde ratio of 1 to 1.1 and 1½% sodium hydroxide as catalyst, 92.7% of the formaldehyde was consumed as compared to 57.8% of the phenol. When the reaction was continued for 22 hours all the formaldehyde was consumed but at this point only 62.9% of the phenol had reacted. Even after 38 hours at 50°C. more than ¼ of the phenol was left unreacted. Another reaction was run at 20°C. using a phenol-to-formaldehyde ratio of 1 to 1.1 with 3% sodium hydroxide as catalyst. At the end of 6.1 days the mix contained 14.95% phenol, or 31.4% of that charged. Even after 53.4 days the mix still contained 11.33% phenol, or about 24% of that charged. These observations are very important from a practical point of view since the unreacted phenol, if left in the resin, will have a strong influence on the properties of the resin. Unfortunately the data on phenol consumption were not analyzed kinetically. In a previous publication Vanscheidt⁶⁶ indicated that the rate of aldehyde binding was proportional to the concentration of catalyst (alkali).

The effect of added salts on the rate of formaldehyde consumption has been studied by Imoto.⁸⁷ With sodium hydroxide and hydrochloric acid the consumption of formaldehyde is unaffected by the addition of sodium or calcium chloride to the reaction mixture. When ammonia was the catalyst the salts had a definite effect on the rate of reaction.

Sprengling and Lewis⁸⁸ have made a study of the dissociation constants of various phenols and phenol alcohols and have been able to correlate these findings with the relative reactivities of the phenols.

Ammonia and Amines

The addition reaction in the presence of ammonia or primary and secondary amines deserves separate treatment, since these catalysts, unlike the strong alkalies, are in themselves capable of reaction with formaldehyde. Ammonia reacts almost instantly with formaldehyde to form hexamethylenetetramine. That compound or an equivalent amount of ammonia may be used interchangeably as a catalyst for the phenol-formaldehyde reaction with equivalent results. Primary or secondary amines may react with phenol and formaldehyde to form phenolic-type Mannich bases and hexamethylenetetramine may form hydroxybenzylamines. (See Chapter 5.) The exact role of the Mannich bases or the hydroxybenzylamines in the phenol-aldehyde reaction is not fully established, but it is known that phenol alcohols may be formed along with the amines.

Nordlander⁸³ was one of the first to make a kinetic study of the reaction of phenol with formaldehyde using ammonia as catalyst. The addition of formaldehyde to the phenol apparently followed first-order kinetics except at very low concentrations of ammonia, where the reaction appeared to change to second order. Unfortunately full details of Nordlander's work were not published. However, the review indicates that Nordlander thought that the primary reaction was limited to the interaction of 1 mole of the formaldehyde with 1 of phenol, no formaldehyde reacting with any of the intermediates. The following expression was developed to relate the rate of reaction with temperature and catalyst concentration:

$$K = \frac{1}{C^{1.38}t} \log \frac{a}{a-x}$$

where C is the catalyst concentration, a is the initial formaldehyde concentration, and $a - x$ is the formaldehyde concentration at time t .

The equation was worked out for a phenol to formaldehyde ratio of 1 to 1.

Yanagita⁶⁹ has also found that the ammonia-catalyzed addition reaction follows apparent first-order kinetics as determined by the disappearance of formaldehyde. The reaction was studied using various ratios of formaldehyde to phenol at 80° and 90°C. The activation energy, calculated from the rate data, was given as 17 kcal. The rate of the addition reaction as well as the time for separation of resin from the reaction mixture was compared with that where hydrochloric acid was used as catalyst. The more rapid formation of resin with the acid catalyst was attributed to the fact that acid favors the formation of dihydroxydiphenylmethanes whereas ammonia favors the formation of phenol alcohols.

Debing⁴⁵ found that his data on the disappearance of formaldehyde fell on a straight line when $\log a/(a - x)$ was plotted against time. This indicates that the reaction follows apparent first-order kinetics. Hexamethylenetetramine was used as catalyst in place of ammonia because of greater ease in handling. The temperature coefficient for the reaction was given as 1.98 for each 10-degree rise in temperature, and the activation energy was calculated at 15.4 kcal., a figure somewhat below that reported by Yanagita.⁶⁹

One of the earliest as well as one the most complete studies on the kinetics of an amine-catalyzed reaction of formaldehyde with various phenols was published by Sprung.⁴⁸ This study covered the reaction of phenol and several of the cresols and xylenols with paraformaldehyde in the absence of added water. Triethanolamine was used as a catalyst because of lack of volatility and because of its ready solubility in the reaction mixture. The rate of formaldehyde disappearance was followed by titration with hydroxylamine hydrochloride. The loss of reactive ring positions, caused by the formation of methylene bridges, was followed by measuring the decrease in "bromine number" of the reaction mixture.

When the data on the disappearance of the formaldehyde were plotted against time on semi-logarithmic paper, a straight line was obtained in most instances, indicating that the addition reaction follows apparent first-order kinetics. The first-order rate constants for various phenols are given in Table IV along with their comparative rates of reaction.

As mentioned earlier, increasing the ratio of paraformaldehyde to phenol caused a decrease in the rate of reaction. With phenol at 98°C. the effect of ratio of reactants is given by the equation

$$K = 0.0069C$$

Table IV

Phenol	Apparent First-Order Rate Constant	Relative Reactivity
3,5-Xylenol	0.0630	7.75
<i>m</i> -Cresol	.0233	2.88
2,3,5-Trimethylphenol	.0121	1.49
Phenol	.00811	1.00
3,4-Xylenol	.00673	0.83
2,5-Xylenol	.00570	0.71
<i>p</i> -Cresol	.00287	0.35
Saligenin	.00272	0.34
<i>o</i> -Cresol	.00211	0.26
2,6-Xylenol	.00130	0.16

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where K is the rate of disappearance of formaldehyde and C is the ratio of phenol to formaldehyde. The average temperature coefficient for the reaction was 1.71 for each 10-degree rise in temperature, and the heat of activation was given as 13.8 kcal.

The action of dilute aqueous triethanolamine appears to be different from that of the anhydrous amine. Sprung found a first-order reaction under anhydrous conditions, and DeJong and DeJonge⁶⁴ found that the reaction obeyed second-order kinetics with aqueous amine. The rate with aqueous amine was exclusively dependent on the concentration of hydroxyl ions and was independent of the concentration of amine.

Acids

The acid-catalyzed reaction of phenols with formaldehyde differs from the base-catalyzed reaction in several respects. Not only the mechanism is different but also the major products of the reaction. With strong alkalies up to a temperature of about 60°C. with most phenols the addition reaction may occur to the almost total exclusion of the condensation reaction. Further, with strong alkalies the condensation reaction is independent of catalyst concentration above a minimum value. On the other hand, both the addition and the condensation reaction are extremely sensitive to the quantity of an acidic catalyst.

Because of the wide difference in the catalytic activity of alkalies on the addition and condensation reaction it is possible, by proper control of conditions, to separate the formation and subsequent condensation of the methylol derivatives in the presence of such catalysts.

Under acidic conditions this is much more difficult, and with the phenols normally used in resin manufacture it is almost impossible, since the phenol alcohols condense almost as soon as formed to higher-molecular-weight products. The only satisfactory way to obtain separate data on the condensation reaction under acidic conditions is to prepare the phenol alcohols by an independent means and study their condensation alone or with other phenols after the addition of acids.

Whitehouse⁷⁰ has estimated that the rate of formaldehyde addition with an alkaline catalyst is roughly twice as rapid as the rate of the subsequent formation of dihydroxydiphenylmethanes, and with an acidic catalyst the condensation reaction is probably more than five times as fast as the addition reaction. Kakiuchi⁷¹ has reported that the ratio of the reaction constants for the addition and condensation reactions in novolac resin formation is 5 to 8. In any event the rate-controlling step in the formation of dihydroxydiphenylmethanes under acidic conditions is the formation of the phenol alcohols or as Kakiuchi^{71,72} claims the activation of the formaldehyde into a carbonium cation, which acts as an intermediate for the formation of the phenol alcohol. It has been observed that the addition reaction, as measured by formaldehyde consumption under acidic conditions, is roughly proportional to the concentration of hydrogen ions in the reaction mixture.¹⁸ With equal molar concentrations of the various acids the rate of reaction is roughly proportional to the ionization constant of the acid.

The consumption of formaldehyde by two xylenols as well as by phenol was measured by Euler and Kispoczy.⁸¹ The constants for the reaction were calculated using the equation

$$K = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

Their data showed fair conformity to second-order kinetics. The rate of reaction for phenol was much greater than for the two xylenols studied. The kinetics of the reaction of formaldehyde with *p*-cresol has also been reported.⁷⁸

A paper has been published by Jones⁸⁹ on the kinetics of the reaction of phenol with formaldehyde using acidic catalysts at 80° and 100°C. and also at 30°C. A glass electrode was used to measure the pH of the system, which was varied between 1 and 3 by the addition of hydrochloric acid. At 80° and 100°C. a linear relation was found between the antilog ($-pH$) and the initial rate of formaldehyde con-

sumption. Catalysis by different acids at the same pH caused similar but not identical rates of reaction. This indicates that at least to a first approximation the rate of reaction is dependent on the concentration of hydrogen ions but that the nature of the anion may have a secondary effect. The reaction generally followed approximate second-order kinetics although at a pH of 2.3 with the temperature at $100^{\circ}C$. there were indications that the reaction was shifting to an order greater than two. Conversely, at $30^{\circ}C$. the reaction approached first-order kinetics. Jones suggested that the decrease in order might be explained by the formation of dialcohols which would be favored at the lower temperature. The heat evolved during the addition of a mole of formaldehyde to one of phenol was given as 4.1 kcal., and for the condensation reaction, which involves the elimination of a mole of water between a methylol group and a ring hydrogen, as 16.9 kcal.

Using the bisulfite method, Yanagita⁶⁹ followed the acid-catalyzed disappearance of formaldehyde during its reaction with phenol. The ratio of formaldehyde to phenol was varied between 0.68 and 1.36 to 1, and the reactions were run at 80° or $90^{\circ}C$. His data on the disappearance of aldehyde conformed to apparent second-order kinetics. An activation energy of 16.5 kcal./mole was given.

The rates of reaction of formaldehyde with phenol, dihydroxydiphenylmethane, p -cresol, and the di- and trinuclear derivatives of p -cresol were compared by Kakiuchi.^{71,72} Hydrochloric acid was employed as catalyst. The work with the di- and trinuclear products was undertaken in an effort to learn why the rate of formaldehyde consumption drops off rapidly near the end of a reaction catalyzed by acidic materials. As anticipated, the rate of reaction was much lower with the di- and trinuclear products than with the starting phenols. A discussion of the possible reasons for this was given.

According to Kagawa and Shirai,⁷⁴ water has a strong influence on the activity of acidic catalysts. Salts appear to have little effect.⁶⁷

The hydroxymethylation of phenols below a pH of 3.6 was found by DeJong and DeJonge to be proportional to the concentration of hydrogen ions in the reaction mixture and to follow second-order kinetics.⁶⁴ The concentration of buffers and salts had no effect on the rate.

Uncatalyzed Reaction

A limited number of phenols are sufficiently reactive that resins may be prepared from them without the use of added catalysts. Resorcinol is outstanding in this respect. It was logical, therefore, that Raff and Silverman^{75,76} should select this phenol for study of the non-catalyzed

reaction of a phenol with formaldehyde. Both the resorcinol and the formaldehyde were carefully purified to remove trace contaminants that might function as catalysts. The addition reaction in the absence of added catalyst was of apparent first order with respect to formaldehyde, with an energy of activation of 19 kcal./mole. The temperature coefficient was 2.3 for each 10-degree rise in temperature and remained essentially constant throughout the reaction and was practically independent of the resorcinol-formaldehyde ratio.

B. CONDENSATION REACTION

Two routes are open for study of the condensation reaction. A phenol alcohol may be prepared by an independent means and its rate of condensation may be measured, or an attempt may be made to follow the condensation step in a phenol-formaldehyde reaction mixture where the condensation reaction is proceeding alongside the formation of new phenol alcohols. The first procedure is more reliable, but the second has the advantage that it more nearly approximates the conditions encountered in the manufacture of commercial resins.

Strong Alkalies

Strong alkalies have a very interesting effect on the condensation reaction. They alter the course of the reaction by decreasing, if not eliminating, the amount of dibenzyl ether linkages formed and by increasing the amount of methylene derivatives formed. Alkalies also appear to cause the elimination of formaldehyde from certain phenol alcohols (see Chapter 4). Data by Barthel,⁷⁷ Ziegler and Zigeuner,⁷⁸ and Freeman and Lewis⁸⁹ indicate that in certain instances the preferred reaction in the presence of aqueous alkalies may be between two methylol groups with the formation of a methylene derivative and the elimination of a mole of formaldehyde and a mole of water. It is also interesting to note that at low concentrations of alkali, such as a few tenths of a per cent of the sodium salt of a phenol alcohol, the condensation reaction is related to the amount of alkali, but, above a rather low minimum value, additional alkali has no further effect on the rate of reaction. Granger⁷⁹ found that the condensation of *o*- and *p*-cresol dialcohol was essentially the same with 1 and with $\frac{1}{20}$ mole of caustic. Goldblum's precipitability data show the same overall results.²⁰ According to Goldblum the rate of resinification depends almost entirely on reaction temperature as long as a minimum quantity of alkali is present. Data on very low concentrations of alkali, where

the rate becomes dependent on the amount of alkali, have been reported by Kammerer.^{80, 81}

One of the most detailed studies of the resinification process from a kinetic point of view has been made by Sprung.⁴⁷ The self-condensation of saligenin with and without catalysts as well as the condensation of saligenin with phenol and with resorcinol has been investigated. Saligenin is an ideal compound for such a study since it has both a reactive methylol group and two reactive ring hydrogens. Many of the runs were made without a solvent, but where a solvent was desired pinacol was used. The data obtained by Sprung have been summarized in Table V, pages 268–269.

The data reveal that in the absence of catalyst the self-condensation of saligenin occurs by an apparent second-order reaction with an activation energy of 20 kcal./mole. It is interesting to note that as much as 80% of the saligenin in an uncatalyzed reaction may be recovered as salireton (2,2'-dihydroxydibenzyl ether) but in the presence of alkalis the compound could not be detected. The reaction in the presence of triethanolamine, sodium hydroxide, or a quaternary ammonium base obeyed first-order kinetics during approximately the first half of the reaction, after which the reaction deviated from first-order kinetics. The product from the alkali-catalyzed self-condensation reaction was a resinous solid. The activation energy for the reaction was 18.5 kcal./mole. The reactions of saligenin with phenol and resorcinol were of second order both in the presence and in the absence of a catalyst or diluent (pinacol). The addition of triethanolamine to the reaction mixture had practically no effect on the rate of reaction in pinacol.

In an earlier paper by Sprung⁴⁸ the reaction of various phenols with paraformaldehyde, using triethanolamine as catalyst, was reported. The condensation reaction was followed by means of bromination data. The study indicated that the condensation reactions were very slow compared to the addition reactions. A rate expression was not derived for this phase of the reaction, but the condensation appeared to be approximately linear with time, indicating a zero-order reaction. The heat of activation for the condensation reaction for *m*-cresol was 15.8 kcal./mole.

Oshima and Imoto⁴⁹ measured the decrease in bromine number for the reactions involving (a) saligenin + saligenin, (b) saligenin + phenol, and (c) saligenin + formaldehyde. Unfortunately the data were not treated kinetically to determine the order of the reaction or rate constants. Nevertheless the paper is very interesting.

The condensation or resinification reaction in the presence of ammonia has received less study than the addition reaction. Nord-

lander¹⁸ studied this phase of the reaction by following the decrease in the "bromine number" of the reaction mixture. The condensation reaction appeared to follow first-order kinetics. The temperature coefficient was much higher than for the addition reaction.

Ammonia

The condensation reaction in the ammonia-catalyzed system causes a rapid loss in water solubility of the reaction products.¹² In this respect the resins prepared with ammonia as catalyst resemble more nearly the resins prepared with acidic catalysts than they do those prepared with sodium hydroxide. The effect of catalyst on water solubility is clearly demonstrated by the precipitability data reported by Goldblum.²⁰ The reason for the rapid loss of water solubility in ammonia resins has been discussed in Chapter 3.

Acids

Several interesting studies of the condensation of a phenol alcohol in the presence of acidic catalysts have been made. Granger¹⁹ studied the condensation of *o*- and *p*-cresol dialcohol as well as the mixed methylol derivatives of phenol. No attempt was made to determine the kinetics of the reaction, but it was noted that the rate of reaction was roughly proportional to the concentration of hydrogen ions in the reaction mixture. In this respect the effect of acids on the addition and condensation reactions is similar although the condensation reaction is the more rapid of the two. Little or no difference in rate of reaction was found between mono- and polyalcohols. This observation should not be considered general, however, since the detailed studies made by Hultsch²¹ show that the reaction of a phenol alcohol devoid of reactive ring positions is much slower than that of a phenol alcohol having free ring positions. This holds both for phenol mono- and phenol dialcohols.

Imoto and Kimura²² have followed the consumption of phenol by reaction with *p*-cresol dialcohol with hydrogen chloride as catalyst. The heat of activation for methylene bridge formation was given as 13.7 kcal./mole; that for dibenzyl ether formation was estimated at 27.4 kcal./mole. The order of reaction was not determined.

Table V. Experimental Results

Reactants	Run No.	Temperature, °C.	Catalyst	Product	Order	Rate Constant, k
Saligenin	60, 65	98.5	None	"Salireton" *	2nd	7.2×10^{-4} kg./mole/min.
Saligenin	11	109	None	"Salireton" *	2nd	1.53×10^{-3} kg./mole/min.
Saligenin	22	119	None	"Salireton" *	2nd	2.64×10^{-3} kg./mole/min.
Saligenin	12	130.5	None	"Salireton" *	2nd	5.96×10^{-3} kg./mole/min.
Saligenin	78, 24	98.5	T.E.A.††	Resin	1st	2.8×10^{-3} /min.
Saligenin	58	98.5	T.E.A.§	Resin	1st	2.25×10^{-3} /min.
Saligenin	59	98.5	T.E.A.	Resin	1st	2.25×10^{-3} /min.
Saligenin	85	110.5	T.E.A.†	Resin	1st	6.1×10^{-3} /min.
Saligenin	82	118	T.E.A.†	Resin	1st	1.07×10^{-2} /min.
Saligenin	14	130.5	T.E.A.†	Resin	1st	1.66×10^{-2} /min.
Saligenin	66	98.5	NaOH †	Resin	1st	2.6×10^{-3} /min.
Saligenin	67	98.5	Q.B.†¶	Resin	1st	2.6×10^{-3} /min.
Saligenin: pinacol (1:2)	5	98.5	None	"Salireton"	2nd	2.35×10^{-4} kg./mole/min.
Saligenin: pinacol (1:1)	48	98.5	T.E.A.	Resin	1st	5.76×10^{-4} /min.
Saligenin: pinacol (1:2)	49	98.5	T.E.A.†	Resin	1st	3.8×10^{-4} /min.
Saligenin: pinacol (1:3)	50	98.5	T.E.A.†	Resin	1st	2.7×10^{-4} /min.
Saligenin: phenol (1:1)	61, 70	98.5	None	Dihydroxydiphenylmethane	2nd	4.1×10^{-4} kg./mole/min.
Saligenin: phenol (1:1)	45, 15	98.5	T.E.A.	Dihydroxydiphenylmethane	2nd	5.13×10^{-4} kg./mole/min.

Saligemin:phenol (1:1)	81	110.5	T.E.A.†	Dihydroxydiphenylmethane	2nd	1.51×10^{-3} kg./mole/min.
Saligemin:phenol (1:1)	84	118	T.E.A.	Dihydroxydiphenylmethane	2nd	2.35×10^{-3} kg./mole/min.
Saligemin:phenol (1:2)	46, 20	98.5	T.E.A.†	Dihydroxydiphenylmethane	2nd	4.51×10^{-4} kg./mole/min.
Saligenin:resorcinol (1:1)	10	98.5	None	Trihydroxydiphenylmethane	2nd	3.28×10^{-3} kg./mole/min.
Saligemin:resorcinol: pinacol (1:1:2)	17	98.5	None	Trihydroxydiphenylmethane	2nd	1.06×10^{-3} kg./mole/min.
Saligemin:resorcinol: pinacol (1:2:2)	19, 25	98.5	None	Trihydroxydiphenylmethane	2nd	1.91×10^{-3} kg./mole/min.
Saligemin:resorcinol: pinacol (2:1:2)	21	98.5	None	Trihydroxydiphenylmethane	2nd	2.18×10^{-3} kg./mole/min.
Saligemin:resorcinol: pinacol (1:1:2)	18	98.5	T.E.A.	Trihydroxydiphenylmethane	2nd	1.18×10^{-3} kg./mole/min.
Saligemin alone for 300 minutes then T.E.A. added	16	98.5	None	"Salireton"	2nd	5.85×10^{-4} kg./mole/min.
		98.5	T.E.A.†	Resin	1st	3.8×10^{-4} /min.

* Salireton is 2,2'-dihydroxydibenzyl ether.

† 0.174 mole/1000 grams.

‡ T.E.A. is triethanolamine.

§ 0.348 mole/1000 grams.

|| 0.696 mole/1000 grams.

¶ Q.B. is tetraethylammonium hydroxide.

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Uncatalyzed Reactions

The uncatalyzed, or purely thermal, condensation of phenol alcohols normally leads to the formation of polyethers as a major product. Certain data already in the literature were treated by Kammerer⁸⁴ in the light of the basic work by Flory on the kinetics of condensation reactions. In a study of the polyesterification reaction Flory found that although the viscosity of a particular reaction mixture changed 2000 fold the rate of the condensation reaction did not change as long as a means for removing the by-products of the reaction was provided.⁸⁵ The esterification of oxyacids or glycols plus a dibasic acid in a melt is a stepwise reaction involving the loss of water. As the hardening of a phenol alcohol is also a stepwise reaction involving the loss of water, Kammerer reasoned that the hardening of a phenol alcohol should be similar kinetically to a polyesterification reaction.

By a treatment similar to Flory's, rate expressions were derived for reactions following first-, second-, and third-order kinetics. Published data were then tested for conformity to the various rate expressions. By this means the hardening of 2,2'-dihydroxy-3,3'-dimethylol-5,5'-dimethyldiphenylmethane was found to follow second-order kinetics at 153–155°C. The data were reported by Euler.⁸⁶ The hardening of hydroquinone dialcohol, based on data taken from Kyrning,⁸⁷ also followed second-order kinetics up to 62% reaction when run at 150°C. even though the alcohol melts at 190–191°C. The hardening of quinone tetraalcohol followed second-order kinetics at 165°C., but at 180°C. a shift towards third-order kinetics was indicated.

Kammerer concluded on the basis of the results presented above that the theory as to the kinetics of the condensation reaction developed by Flory was applicable to the polyetherification of phenol alcohols. He also concluded that the reactivity of a functional group was unaffected by the size of the molecule and that the functional groups of a given phenol alcohol molecule do not react with each other; e.g., they build no ring compounds.

Kammerer later made a detailed study of the condensation of *p*-cresol dialcohol.^{80, 88} In a platinum or silver vessel the rate of reaction was the same and depended on the purity of the dialcohol. The rate of condensation in air was different from that in nitrogen. Using very pure *p*-cresol dialcohol and very carefully controlled conditions it was possible to split out almost exactly 1 mole of water with essentially no loss of formaldehyde. The reaction was run at 130°C. The reaction followed first-order kinetics between 40 and 240 minutes. During the

first 40 minutes there was some deviation; this was attributed to the fact that reaction was taking place largely in the solid state. Traces of sodium salt, present as a result of preparation of the dialcohol via its sodium salt, had a strong effect on the rate of loss of water and also catalyzed the loss of formaldehyde. As little as 0.36% of sodium almost doubled the amount of water evolved in 100 minutes. A similar study also was made of condensation of trimethylolphenol.⁸¹

Studies on the purely thermal hardening of phenol alcohols have been reported by other workers, but the data were not treated kinetically.^{89, 90}

REFERENCES FOR CHAPTER 10

- ¹ R. Dubrisay and R. Papault, *Compt. rend.*, **215**, 348-350 (1942).
- ² B. Jablonower, *J. Am. Chem. Soc.*, **35**, 811 (1913).
- ³ B. A. Lomakin and V. I. Guseva, *Plasticheskie Massy*, **2**, 281-296, 796 (1937).
- ⁴ S. Tsuruta, *J. Soc. Chem. Ind. Japan*, **39**, 918 (1936).
- ⁵ Suzita and S. Tsuruta, *J. Soc. Chem. Ind. Japan*, Supp. Building, **40**, 419 (1937).
- ⁶ S. Tsuruta, *J. Soc. Chem. Ind. Japan*, Supp. Binding, **44**, 57-58 (1941).
- ⁷ Z. V. Veldenbaum and E. S. Medvedkov, *Org. Chem. Ind. U.S.S.R.*, **6**, 437 (1939).
- ⁸ L. Bettelheim and K. W. Nihlberg, *Brit. Plastics*, **20**, 50, 108 (1948).
- ⁹ S. Tsuruta and M. Fukumura, *J. Soc. Chem. Ind. Japan*, **44**, 812-813 (1941).
- ¹⁰ E. S. Medvedkov and B. M. Polyatskina, *Prom. Org. Khim. U.S.S.R.*, **7**, 232 (1940).
- ¹¹ J. Novak and V. Čech, *Ind. Eng. Chem.*, **20**, 796 (1928).
- ¹² J. Novak and V. Čech, *Ind. Eng. Chem.*, **24**, 1275 (1932).
- ¹³ K. Oshima, *J. Soc. Chem. Ind. Japan*, Supp. Binding, **45**, 129-132, 132-134 (1942).
- ¹⁴ A. Schmid and G. de Senarclens, *Helv. Chim. Acta*, **16**, 10 (1933).
- ¹⁵ S. R. Finn and L. R. Rogers, *J. Soc. Chem. Ind. London*, **67**, 51-57 (1948).
- ¹⁶ F. S. Granger, *Ind. Eng. Chem.*, **29**, 1305-1308 (1937).
- ¹⁷ E. L. Holmes and N. J. L. Megson, *J. Soc. Chem. Ind. London*, **52**, 415-418T (1933).
- ¹⁸ N. J. L. Megson, *J. Soc. Chem. Ind. London*, **57**, 189-197 (1938).
- ¹⁹ N. J. L. Megson, *Brit. Plastics*, August, 1948.
- ²⁰ K. B. Goldblum, Preprint *Bull., Div. Paint, Varnish, and Plastics Chem.*, American Chemical Society Meeting, September, 1950, pp. 60-67.
- ²¹ K. Oshima, *J. Soc. Chem. Ind. Japan*, Supp. Binding, **45**, 155-158 (1942).
- ²² E. Manegold and W. Petzoldt, *Kolloid-Z.*, **95**, 59-69 (1941).
- ²³ M. N. Fineman and I. E. Puddington, *Chemie (Prague)*, **3**, 127-131 (1948).
- ²⁴ M. N. Fineman and I. E. Puddington, *Can. J. Research*, **25B**, 101-107 (1947).
- ²⁵ M. N. Fineman and I. E. Puddington, *Ind. Eng. Chem.*, **39**, 1288 (1947).
- ²⁶ H. F. Müller and I. Müller, *Kunststoffe*, **42**, 57-63 (1952).

- ²⁷ N. J. L. Megson and H. M. Paisley, *J. Soc. Chem. Ind. London*, **58**, 213-215 (1939).
- ²⁸ R. A. Barkhuff and T. S. Carswell, *Ind. Eng. Chem.*, **86**, 461-466 (1944).
- ²⁹ S. Turuta and O. Sugito, *J. Soc. Chem. Ind. Japan*, Supp. Binding, 1940, 319-321.
- ³⁰ A. Bring, *Khim. Prom.*, **1**, (26), 272-277 (1951).
- ³¹ J. I. DeJong, *Rec. trav. chim.*, **72**, No. 4, 356 (1953).
- ³² J. F. Walker, *Formaldehyde*, Reinhold Publishing Corp., New York, 1944, pp. 255-275.
- ³³ B. W. Nordlander, *Oil, Paint, Drug Repr.*, **130**, 3, 27 (Sept. 14, 1936).
- ³⁴ K. Oshima and E. Imoto, *Chem. High Polymers (Japan)*, **8**, 57-60 (1946).
- ³⁵ A. Vanscheidt, A. Itenberg, and G. Shtraikhman, *Narodnyi Komissariat Tyazheloi Prom., S.S.S.R., Sbornik*, **2**, 145-149 (1937).
- ³⁶ A. A. Vanscheidt and A. A. Vasiliev, *J. Applied Chem. U.S.S.R.*, **19**, 7 (1946).
- ³⁷ J. J. Smith, F. M. Rugg, and H. M. Bowman, *Anal. Chem.*, **24**, 497 (1952).
- ³⁸ J. H. Freeman, *Anal. Chem.*, **24**, 2001 (1952).
- ³⁹ J. H. Freeman and C. W. Lewis, *J. Am. Chem. Soc.*, **76**, 2080-2087 (1954).
- ⁴⁰ G. R. Sprengling and J. H. Freeman, *J. Am. Chem. Soc.*, **72**, 1982 (1950).
- ⁴¹ M. Imoto, H. Kakiuchi, and S. Kondo, *J. Inst. Polytech. Osaka*, **2**, No. 2 (1952); Series C, **3**, 107-111 (1952).
- ⁴² J. Haslam, S. M. A. Whettem, and G. Newland, *Analyst*, **78**, No. 927, 340-347 (1953).
- ⁴³ T. Takatani, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **54**, 381-383 (1951).
- ⁴⁴ H. F. Müller and I. Müller, *Kunststoffe*, **38**, 221 (1948).
- ⁴⁵ L. M. Debing, G. E. Murray, and R. J. Schatz, *Ind. Eng. Chem.*, **44**, 354-356 (1952).
- ⁴⁶ L. M. Debing, G. E. Murray, and R. J. Schatz, *Ind. Eng. Chem.*, **44**, 356-359 (1952).
- ⁴⁷ M. M. Sprung and M. T. Gladstone, *J. Am. Chem. Soc.*, **71**, 2907-2913 (1949).
- ⁴⁸ M. M. Sprung, *J. Am. Chem. Soc.*, **63**, 334-343 (1941).
- ⁴⁹ K. Oshima and E. Imoto, *Chem. High Polymers*, **1946**, 51-56.
- ⁵⁰ R. Dubrisay and R. Papault, *Inds. plastiques*, **1**, 132 (1945).
- ⁵¹ H. von Euler and S. V. deKispeczy, *Z. physik. Chem.*, **A189**, 109 (1941).
- ⁵² A. W. Francis, *J. Am. Chem. Soc.*, **48**, 1631 (1926).
- ⁵³ M. M. Sprung, *Ind. Eng. Chem., Anal. Ed.*, **13**, 35-38 (1941).
- ⁵⁴ I. W. Ruderman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 753-759 (1946).
- ⁵⁵ E. Imoto and T. Kimura, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **53**, 9-11 (1950).
- ⁵⁶ C. Jacque and L. Jacque, *Inds. plastiques*, **4**, No. 1, 35-36 (1948).
- ⁵⁷ R. W. Martin, *Anal. Chem.*, **23**, 883-884 (1951).
- ⁵⁸ H. F. Müller and I. Müller, *Kunststoffe*, **41**, 186-188 (1951).
- ⁵⁹ T. T. Jones, *J. Soc. Chem. Ind.*, **65**, No. 9, 264-275 (1946).
- ⁶⁰ K. B. Goldblum, *J. Soc. Chem. Ind.*, **69**, 102-103 (1950).
- ⁶¹ K. Vesely, *Chem. Listy*, **40**, 263-266 (1946).
- ⁶² K. Oshima and E. Imoto, *Chem. High Polymers*, **3**, 60-65 (1946).
- ⁶³ F. C. Stults, R. W. Moulton, and J. L. McCarthy, *Chem. Eng. Progress Symposium*, Ser. 48, No. 4, Reaction Kinetics Transfer Processes, 38-50 (1952).
- ⁶⁴ J. I. DeJong and J. DeJonge, *Rec. trav. chim.*, **72**, 497 (1953).

- ⁶⁶ A. A. Vanscheidt, *Grg. Chem. Ind. U. S. S. R.*, 1937, 385-393.
- ⁶⁸ A. A. Vanscheidt and R. I. Gruz, *Zhur. Priklad. Khim. (J. Applied Chem.)*, 21, 502-511 (1948).
- ⁶⁷ E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 52, 244-247 (1949).
- ⁶⁸ G. R. Sprengling and C. W. Lewis, Preprint Bull., *Div. Paint, Varnish and Plastics Chem.*, American Chemical Society Meeting, September, 1952, p. 77; *J. Am. Chem. Soc.*, 75, 5709 (1953).
- ⁶⁹ M. Yanagita, *J. Soc. Chem. Ind. Japan*, 45, 1086-1090 (1942).
- ⁷⁰ A. A. K. Whitehouse, *Ann. Repts. Soc. Chem. Ind.*, 32, 268-278 (1947).
- ⁷¹ H. Kakiuchi, *Chem. High Polymers (Japan)*, 8, 29-43 (1951).
- ⁷² H. Kakiuchi, *J. Inst. Polytech., Osaka*, 2, No. 2 (1952).
- ⁷³ H. Dostal and R. Raff, *Z. physik. Chem.*, B32, 117-129 (1936).
- ⁷⁴ I. Kagawa and Z. Shirai, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 54, 64-66 (1951).
- ⁷⁵ R. A. V. Raff and B. H. Silverman, *Ind. Eng. Chem.*, 43, 1423-1427 (1951).
- ⁷⁶ R. A. V. Raff and B. H. Silverman, *Can. J. Chem.*, 29, 857-862 (1951).
- ⁷⁷ R. Barthel, *Plastica (Holland)*, 2, 247-251 (1949).
- ⁷⁸ E. Ziegler and G. Ziegeuner, *Kunststoffe*, 39, 191-192 (1949).
- ⁷⁹ F. S. Granger, *Ind. Eng. Chem.*, 29, 860, 1125 (1937).
- ⁸⁰ H. Kammerer, *Die Makromolekulare Chem.*, 8, Pt. 1, 98-109 (1952).
- ⁸¹ H. Kammerer and M. Grossman, *Angew. Chem.*, 65, 263 (1953).
- ⁸² H. F. Müller and I. Müller, *Kunststoffe*, 38, 25-44 (1948).
- ⁸³ K. Hultsch, *Kunststoffe*, 37, 205-208 (1947).
- ⁸⁴ H. Kammerer, *Die Makromolekulare Chem.*, 8, 72-84 (1952).
- ⁸⁵ P. J. Flory, *J. Am. Chem. Soc.*, 61, 3334 (1939); 59, 466 (1937).
- ⁸⁶ H. von Euler, E. Adler, and B. Bergstrom, *Arkiv Kemi Mineral. Geol.*, B14, No. 25, 1-6 (1941).
- ⁸⁷ S. Kyrning, *Arkiv Kemi Mineral. Geol.*, B15, No. 11, 1-8 (1941).
- ⁸⁸ H. Kammerer, *Die Makromolekulare Chem.*, 8, Pt. 1, 85-96 (1952).
- ⁸⁹ A. Zinke, E. Ziegler, and I. Hontschik, *Monatsh.*, 78, 317-324 (1946).
- ⁹⁰ E. Schauenstein and S. Bontempo, *Ber.*, 76, 75-80 (1943).

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